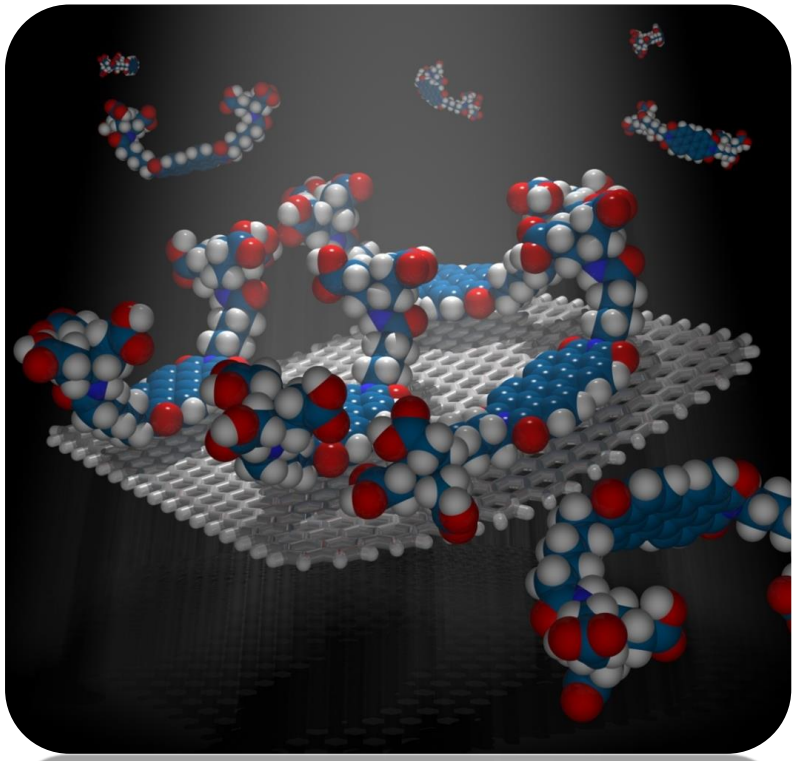
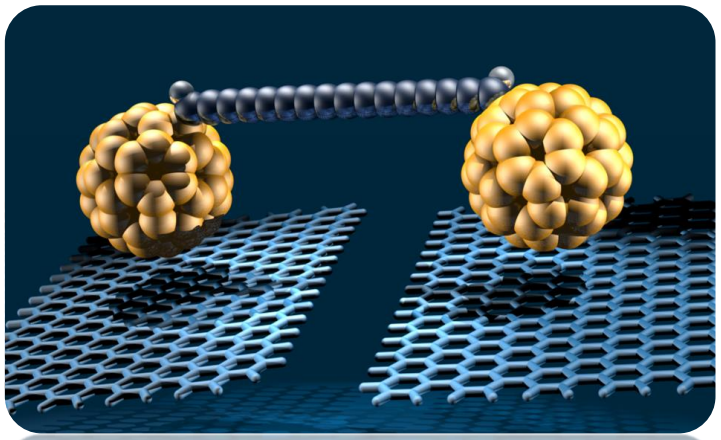
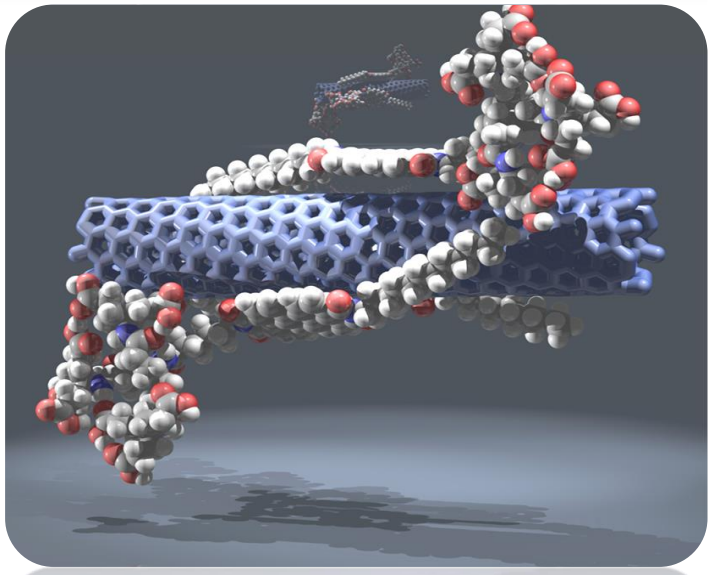
Chemical Functionalization of Synthetic Carbon Allotropes



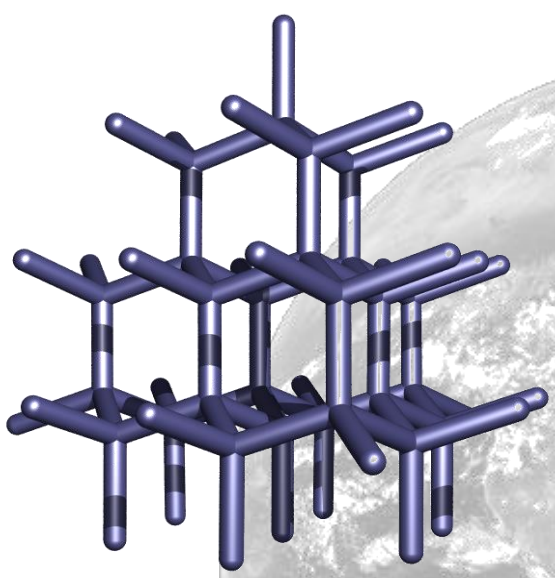


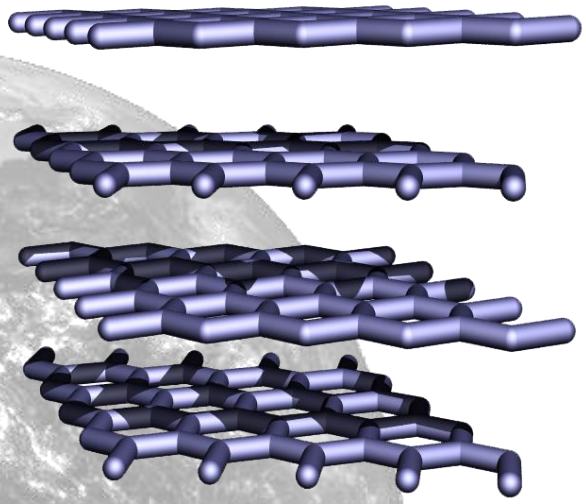


Carl Friedrich Gauß-Kolloquium 2014
Braunschweig
Andreas Hirsch
09. 05. 2014

SCA Synthetic Carbon Allotropes SFB953

The World of Carbon

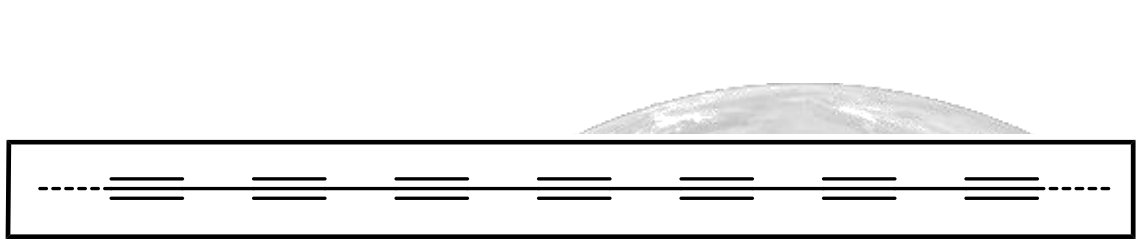




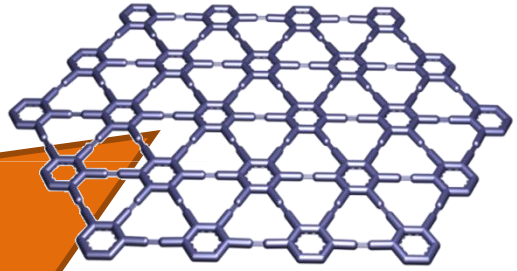
Diamond

Graphite

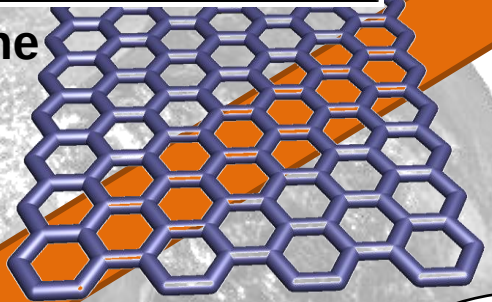
Synthetic Carbon Allotropes



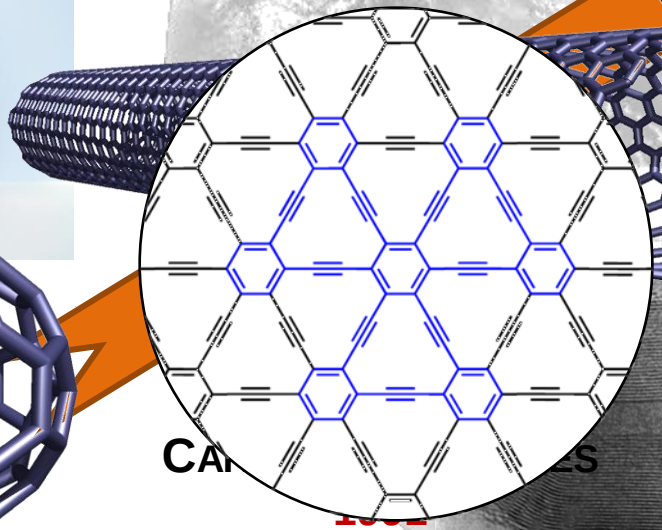
1-dimensional - sp-carbyne

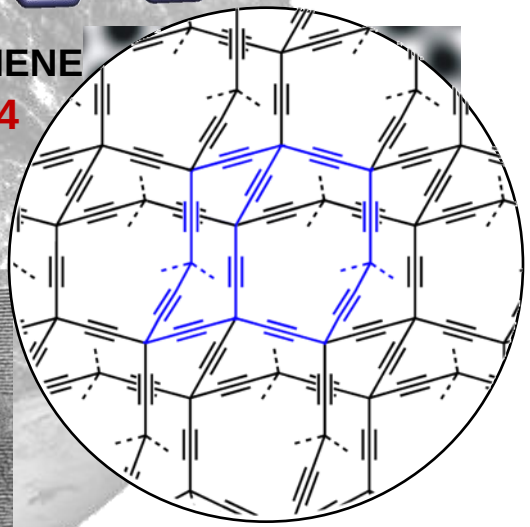


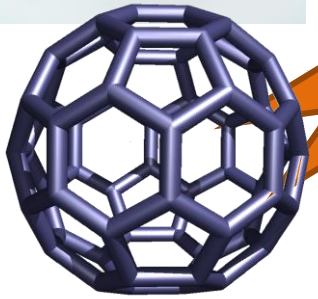
MANY UNDISCOVERED ALLOTROPES
2012 and beyond



GRAPHENE
2004







FULLERENES
1985/1990

2-dimensional
sp-sp^2-graphyne

3-dimensional
sp-sp^3-yne-diamond

SCA
Synthetic Carbon Allotropes SFB953

Chemistry, Functionalization, Derivatives

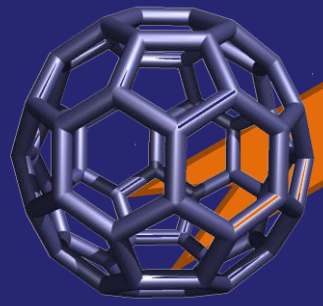
almost unexplored

? ? ?

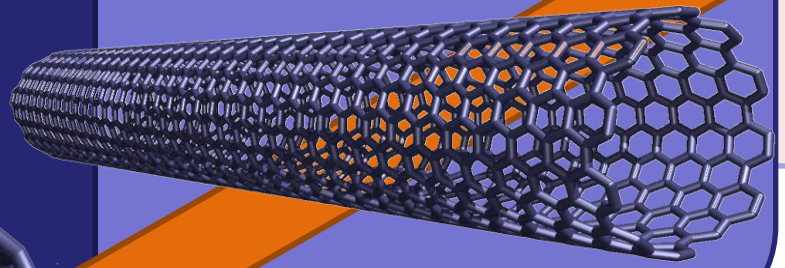
first examples of covalent and non–covalent functionalization

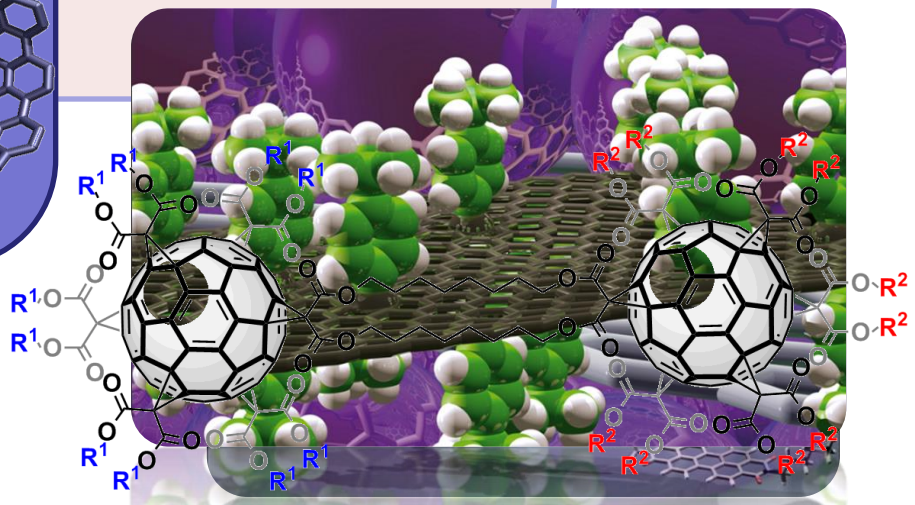
selectivity of reactions still poor

many well defined derivatives synthesized and reactivity principles discovered



few cluster modifications





The World of Carbon

Fullerenes
1985

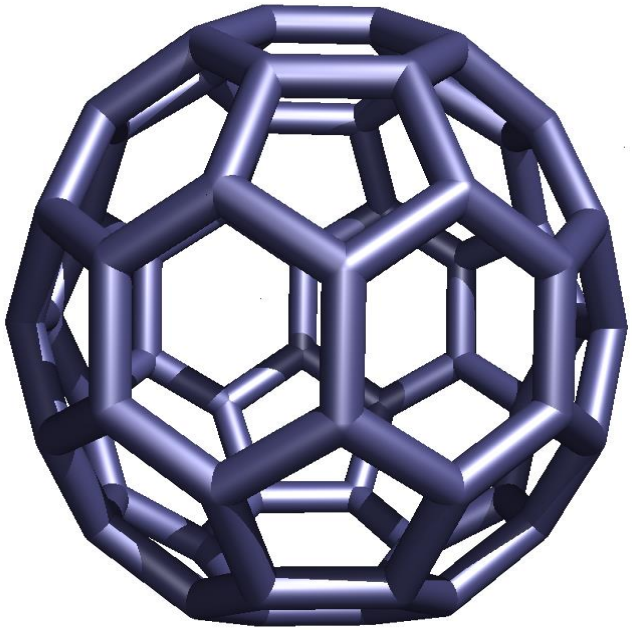
Carbon Nanotubes
1991

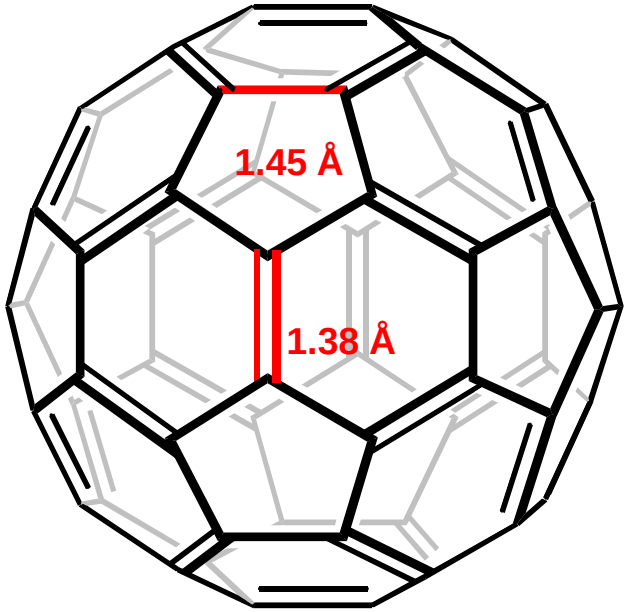
Graphene
2004

many undiscovered allotropes
e.g. sp-sp^2-Graphyne
> 20??

SCA
Synthetic Carbon Allotropes SFB953

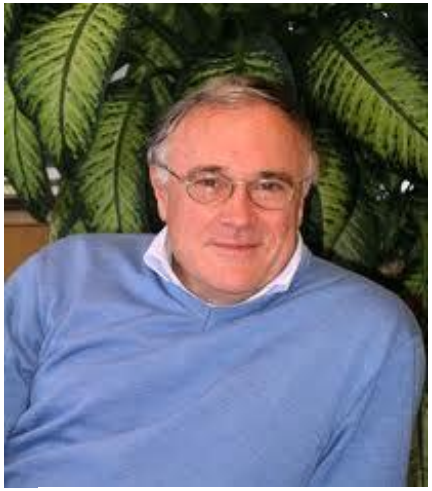
Fullerenes

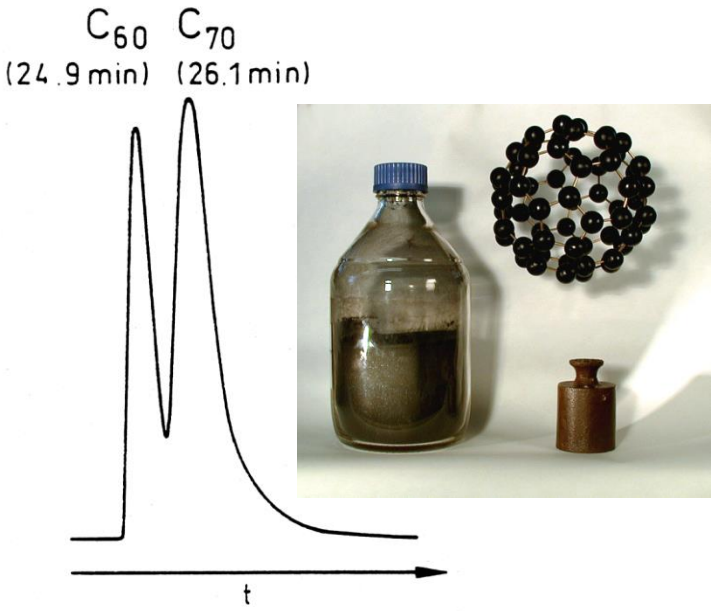




Klaus Müllen and the Fullerenes

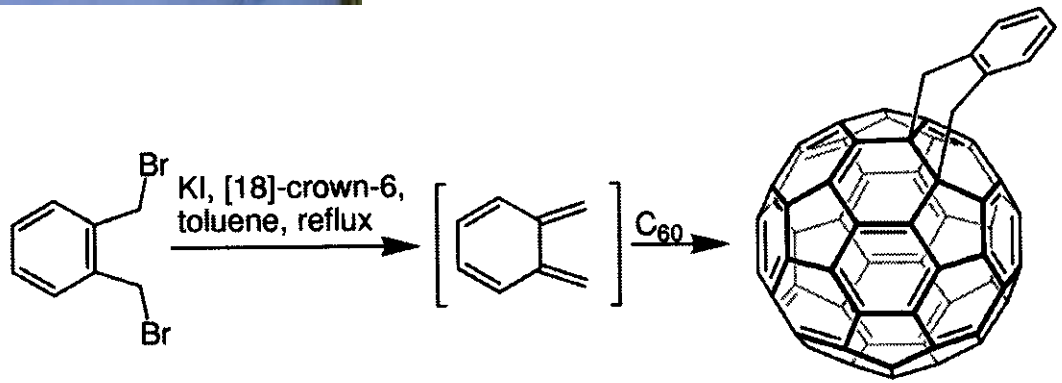
Large scale separation of pure fullerenes





polystyrene as stationary phase

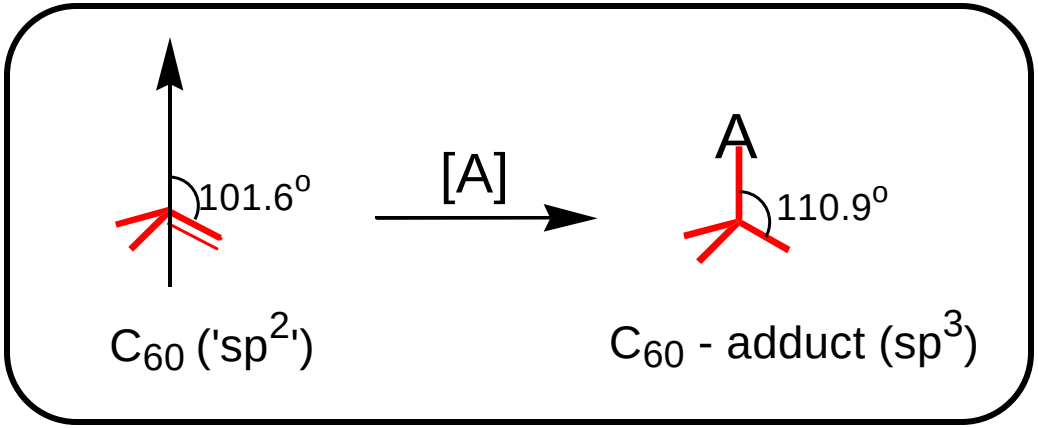
Fullerene Chemistry



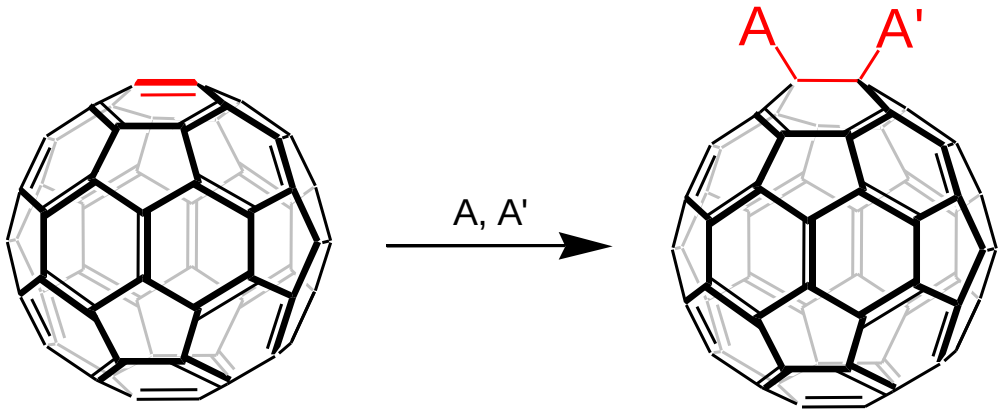
Diels-Alder-reactions

A. Gügel, K. Müllen, at al. *Angew. Chem*. **1992**, *104*, 666.
P. Belik, A. Gügel, J. Spikermann, K. Müllen, *Angew. Chem*. **1993**, *105*, 95

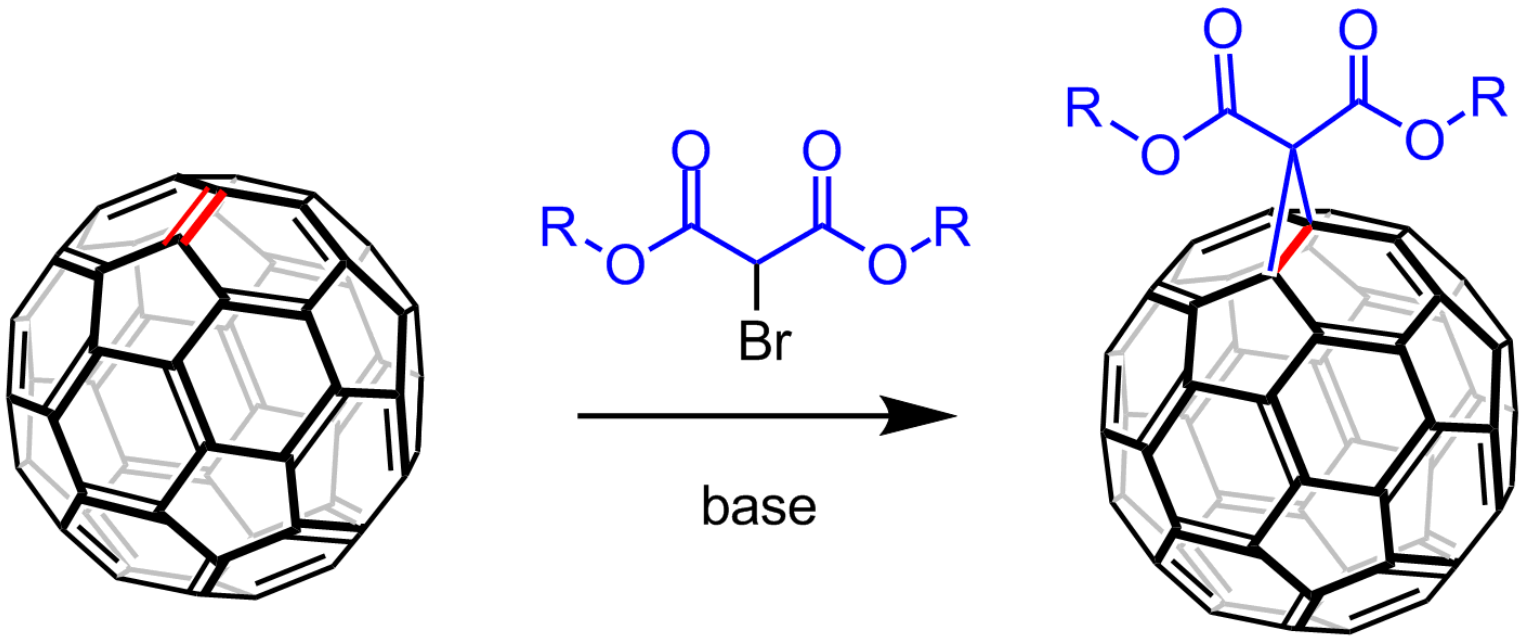
Fullerenes



- relief of strain energy by about 10 kcal/mol per double bond
- reactive outer surface, rich exohedral addition chemistry



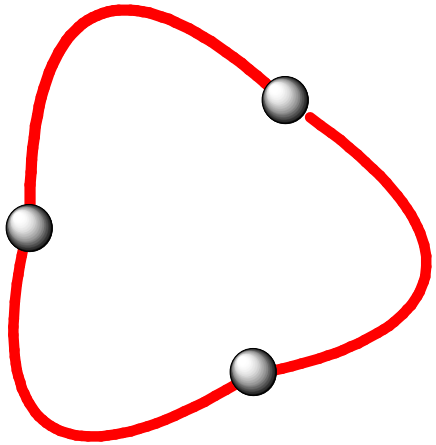
Nucleophilic cyclopropanation of C_{60}



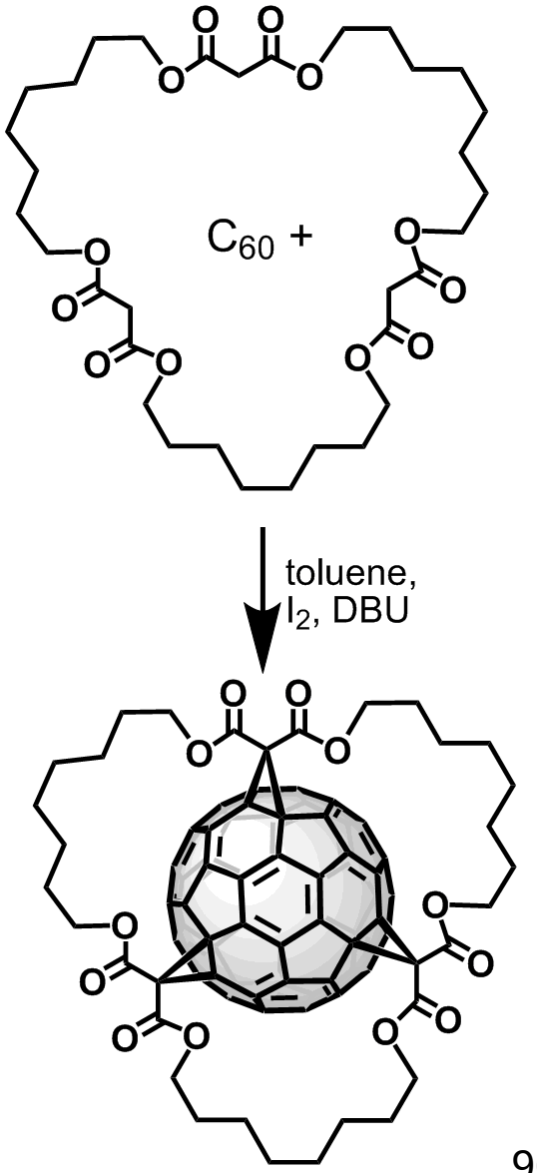
R = broad variety of groups including functional units

Fullerenes

C8-spacer

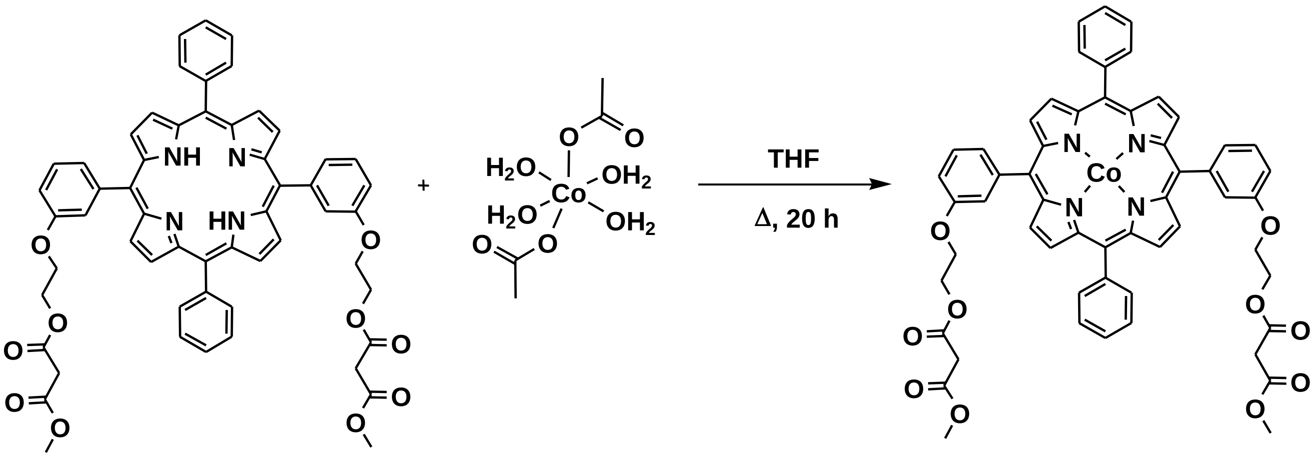


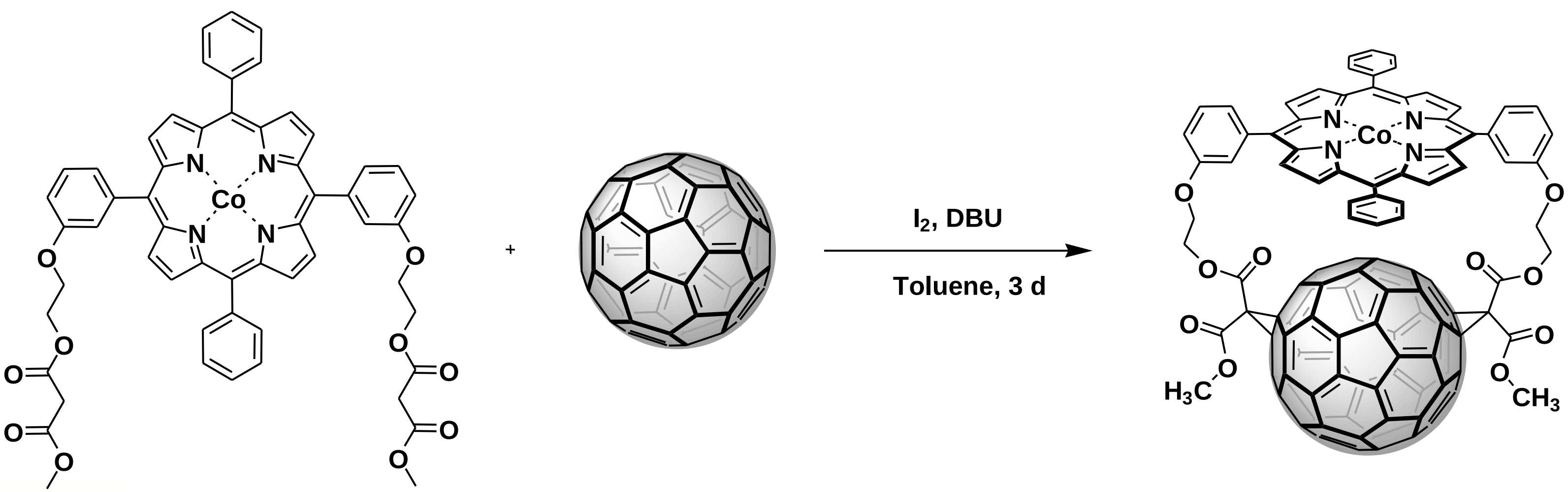
trisfunctional macrocycle



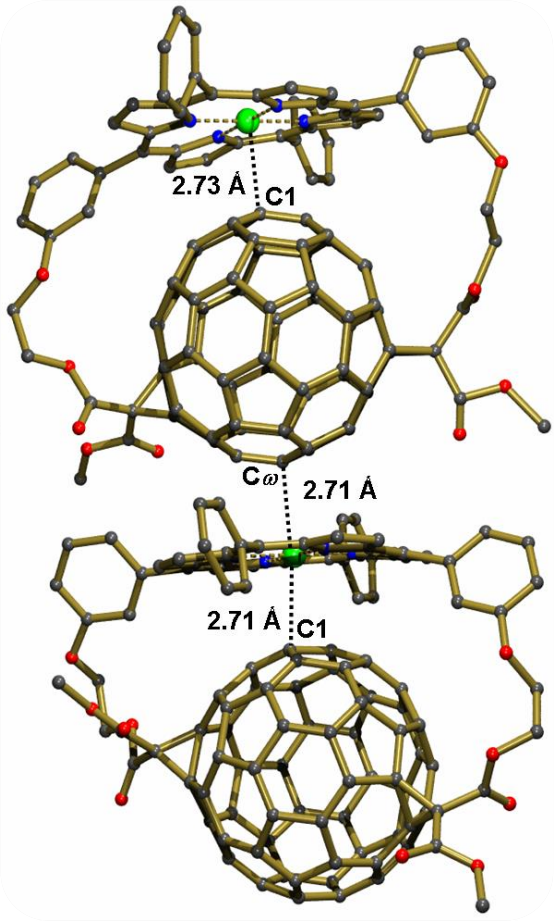
96% ***e,e,e***

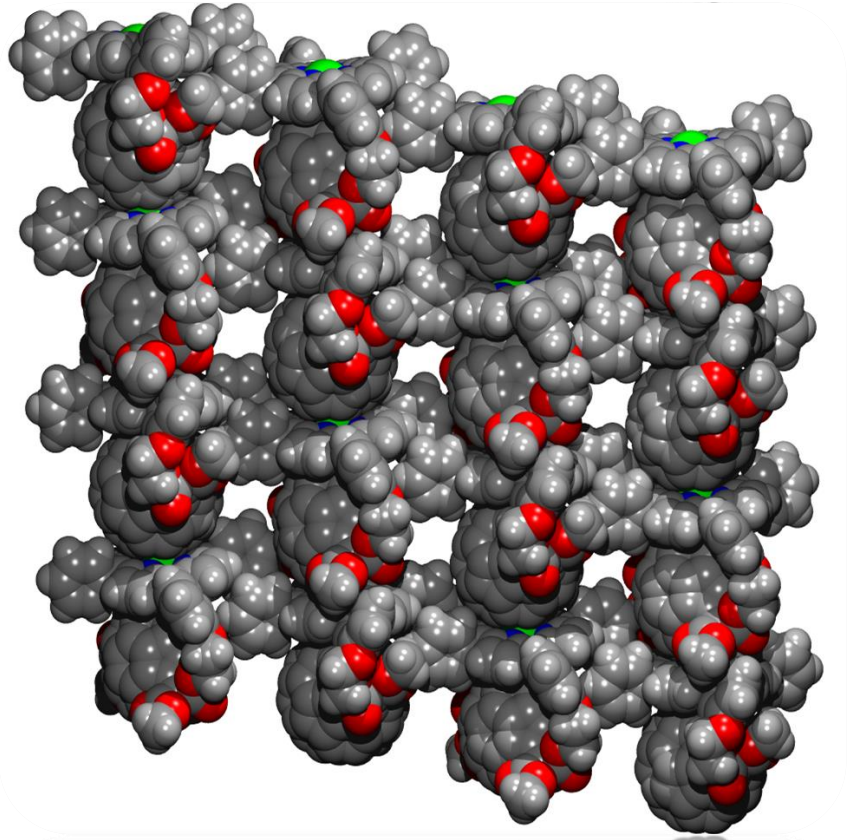
Fullerenes


NH
N
N
HN
+
H_2O
OH_2
Co
H_2O
OH_2
O
THF
Δ, 20 h
N
N
Co
N
N

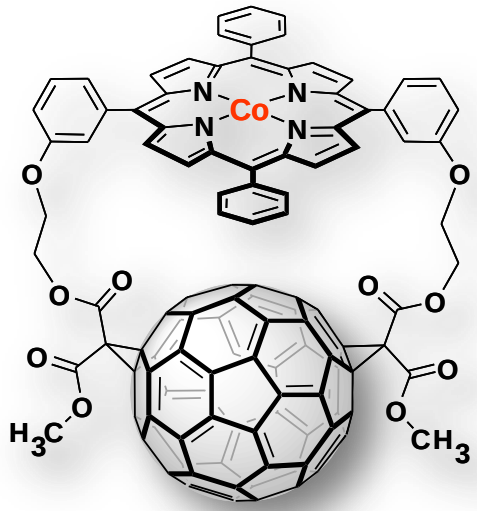

N
N
Co
N
N
+
I_2, DBU
Toluene, 3 d
Co
H_3C
CH_3

Coordination polymers (M = Co, Cu)

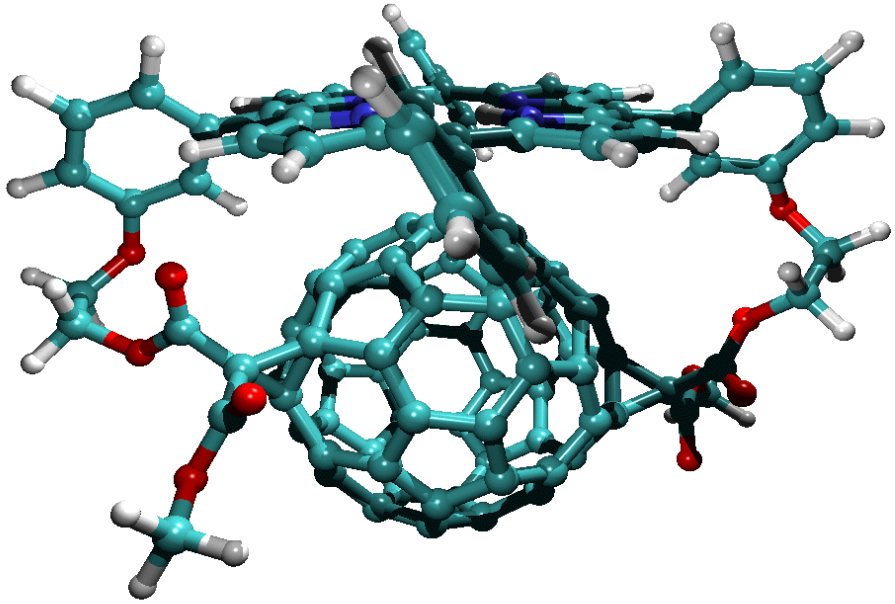




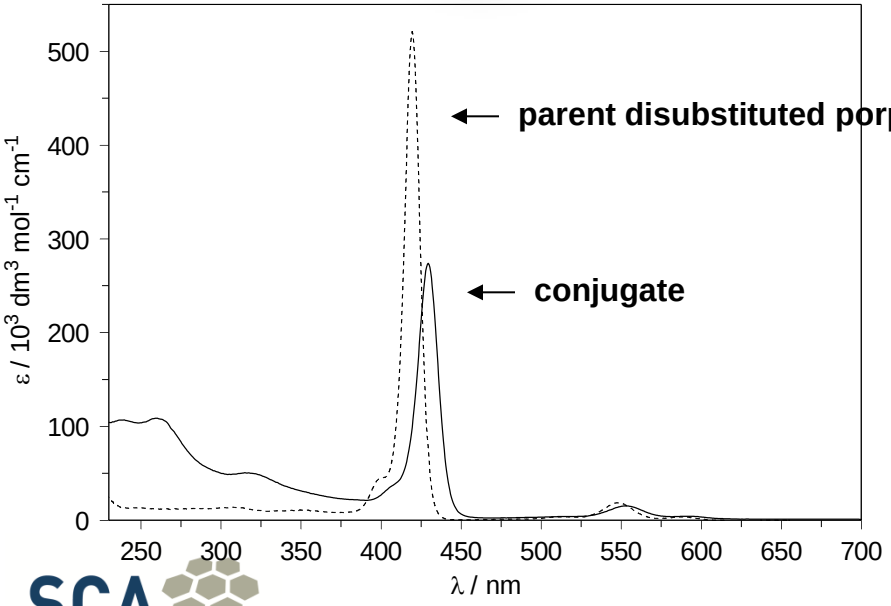
Fullerenes



trans-2



shortest interplanar MM3-distance 2.9 Å



Photoiduced electron transfer

porphyrine to fullerene

back electron transfer: Marcus-Inverted region

$\tau_{toluene}$: 619 ps

τ_{THF}: 385 ps

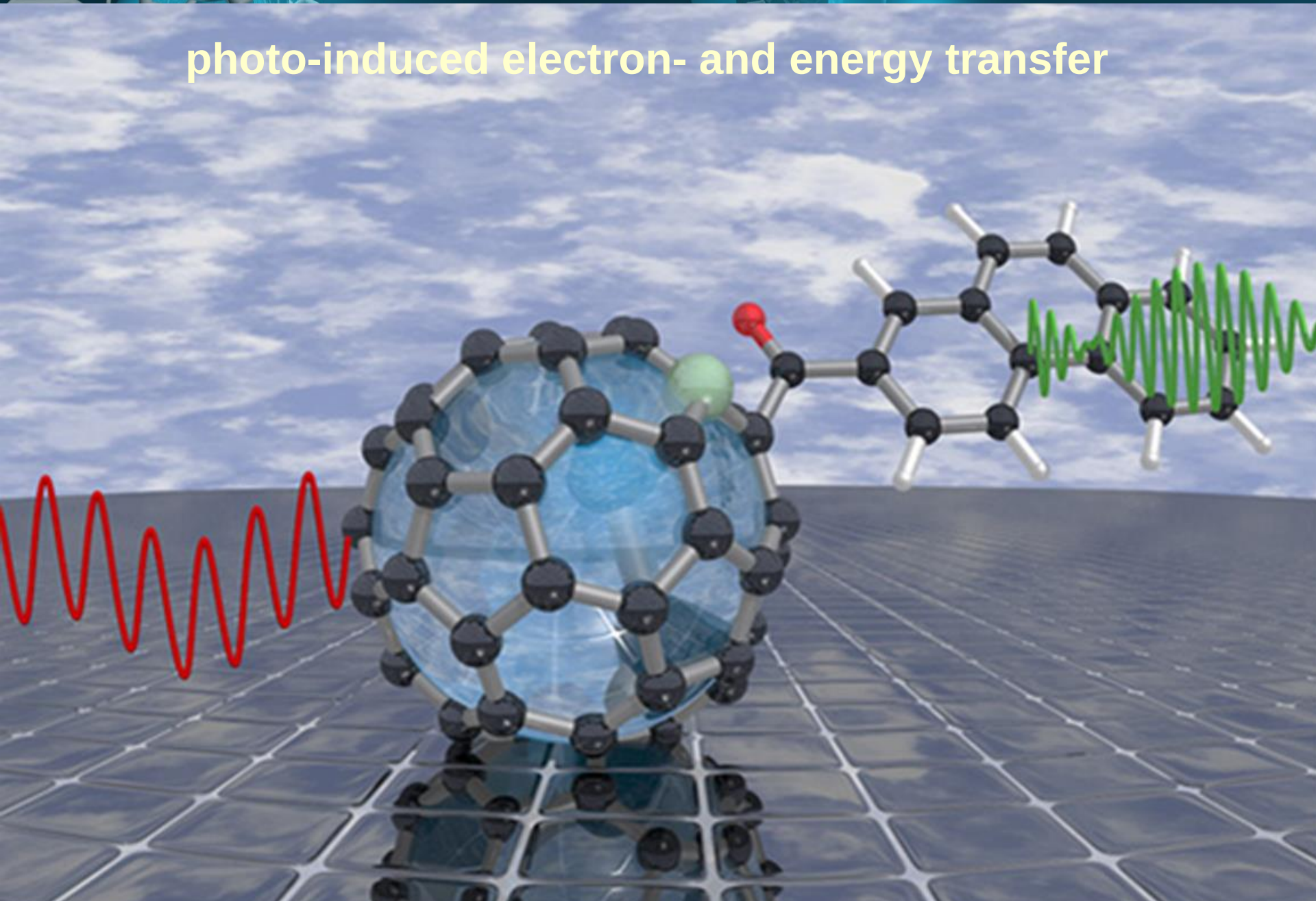
$\tau_{methylenechloride}$: 121 ps

$\tau_{benzonitrile}$: 38 ps

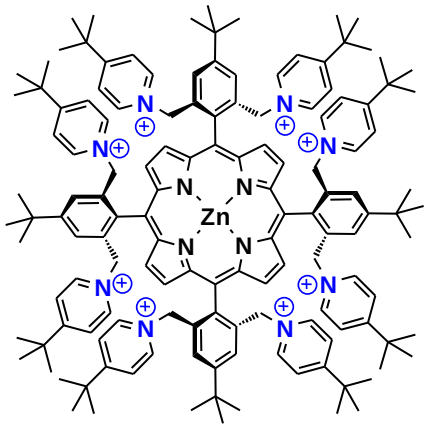
Fullerenes

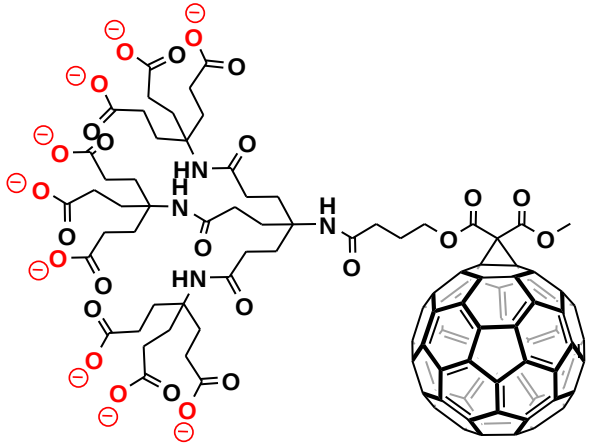
FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

photo-induced electron- and energy transfer

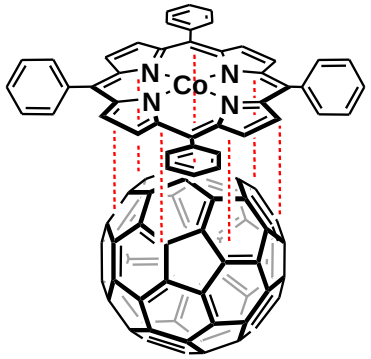


Fullerenes



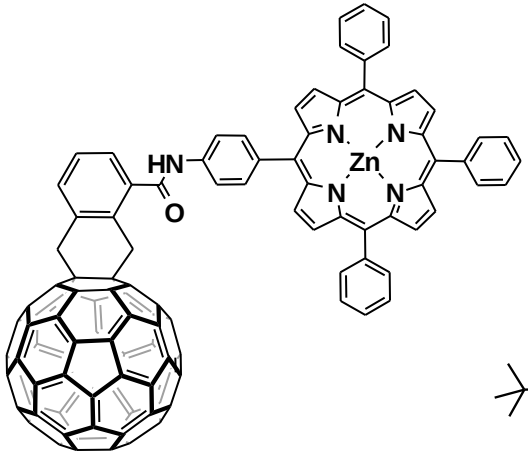


electrostatic

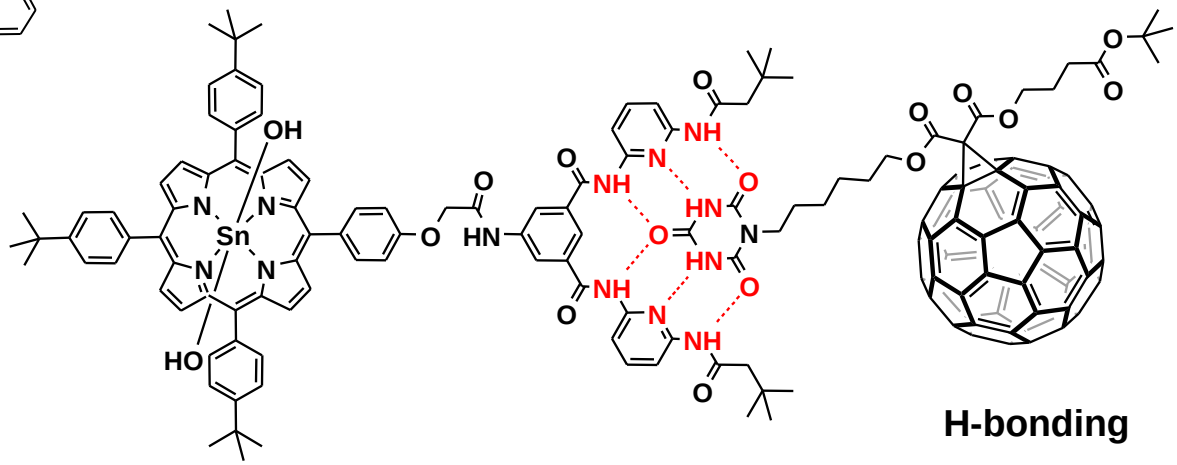


π-stacking

binding motifs
in C_{60} based dyads

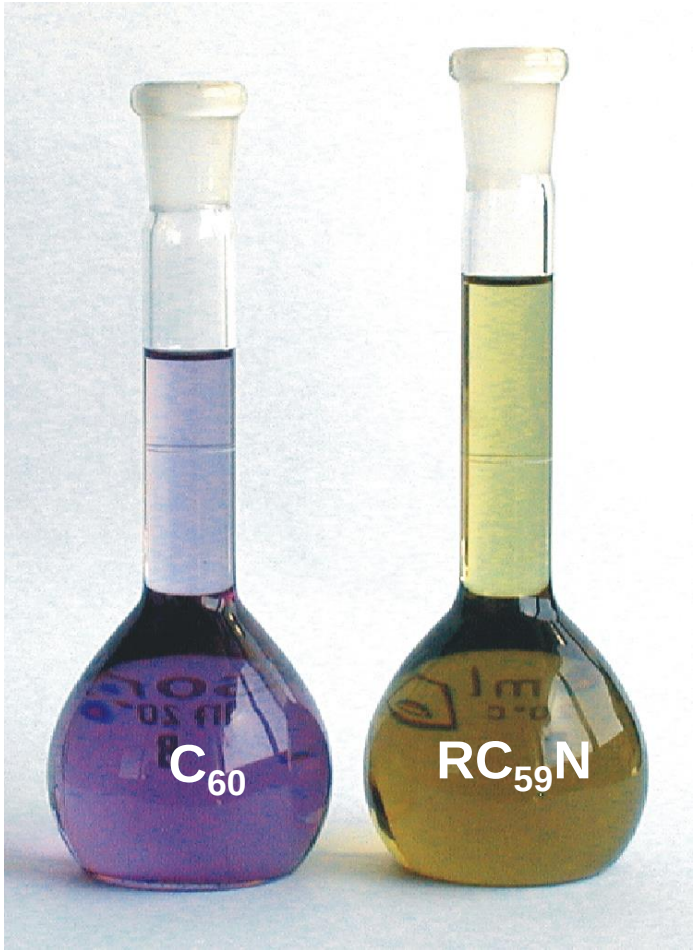


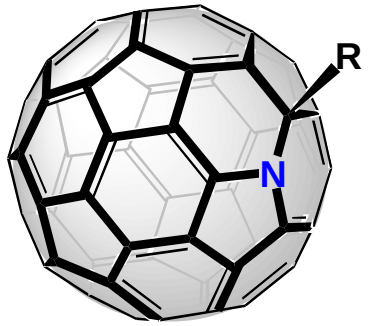
covalent



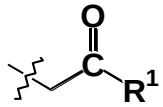
H-bonding

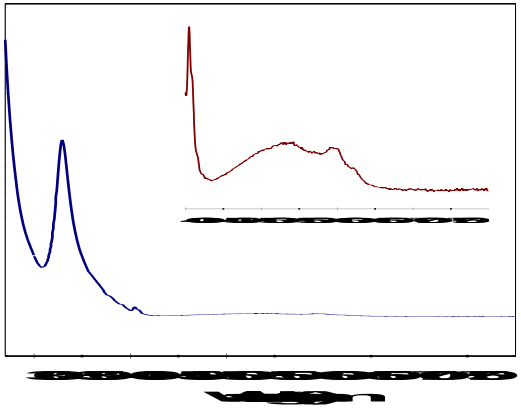
Heterofullerenes

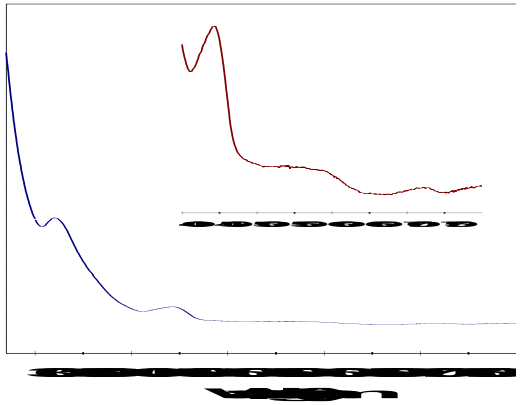




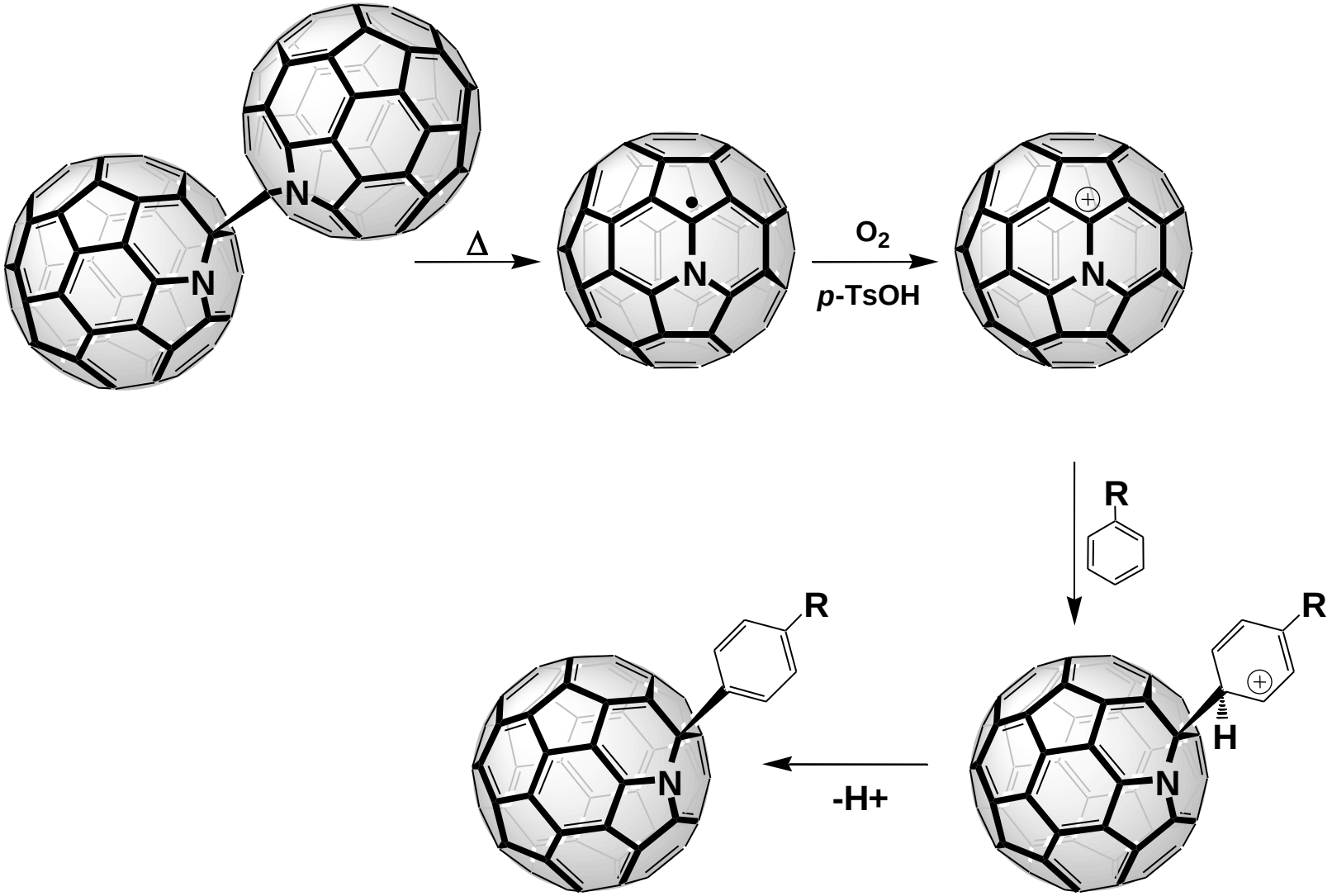
R = $C_{59}N$, H, Ar,



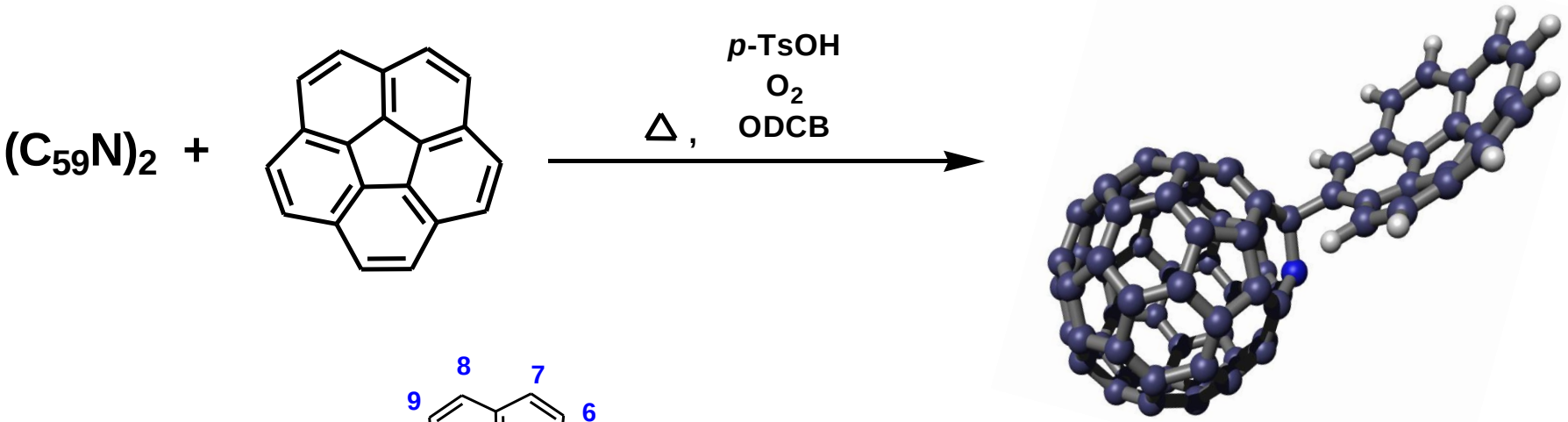


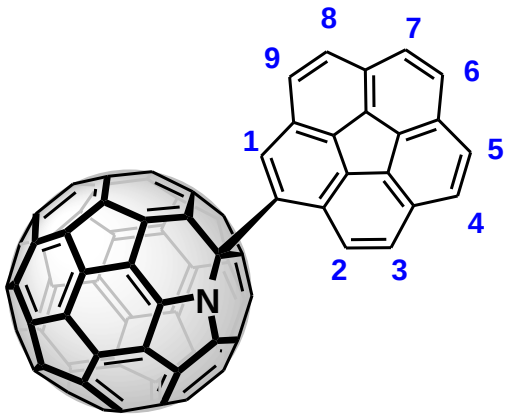


Heterofullerenes

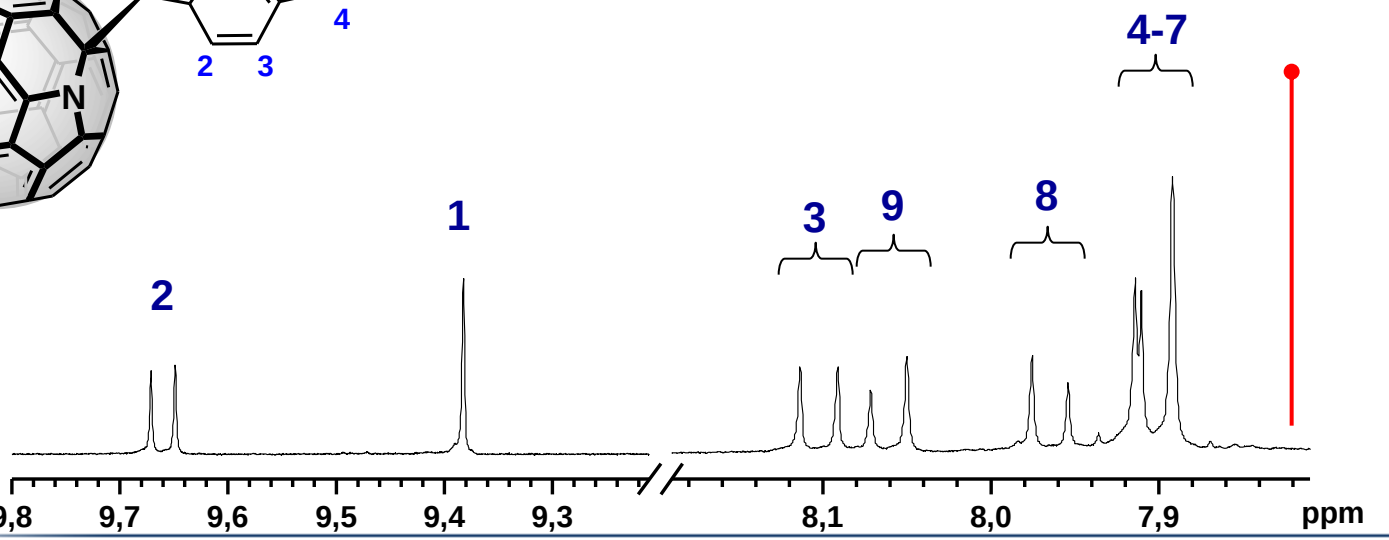


Heterofullerenes



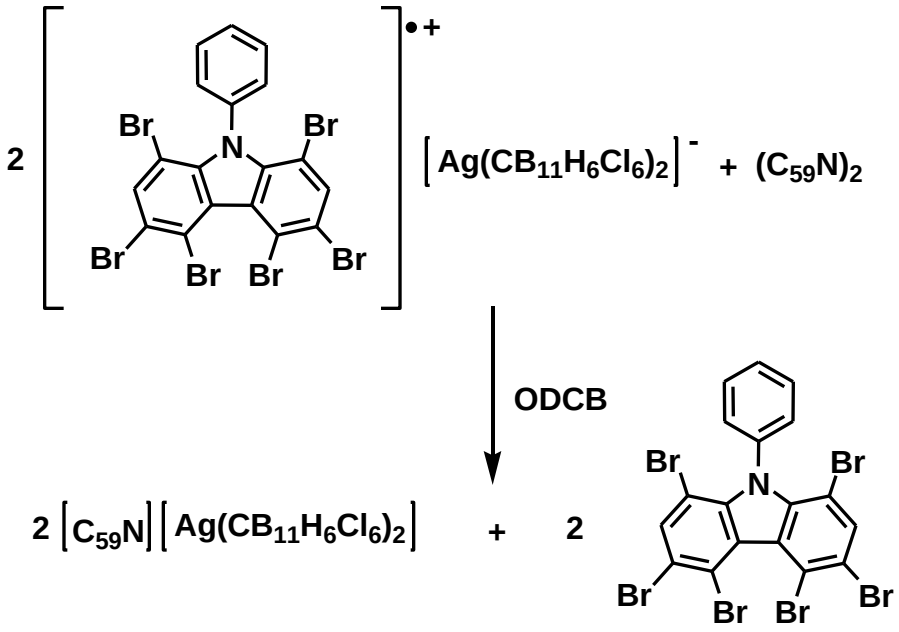


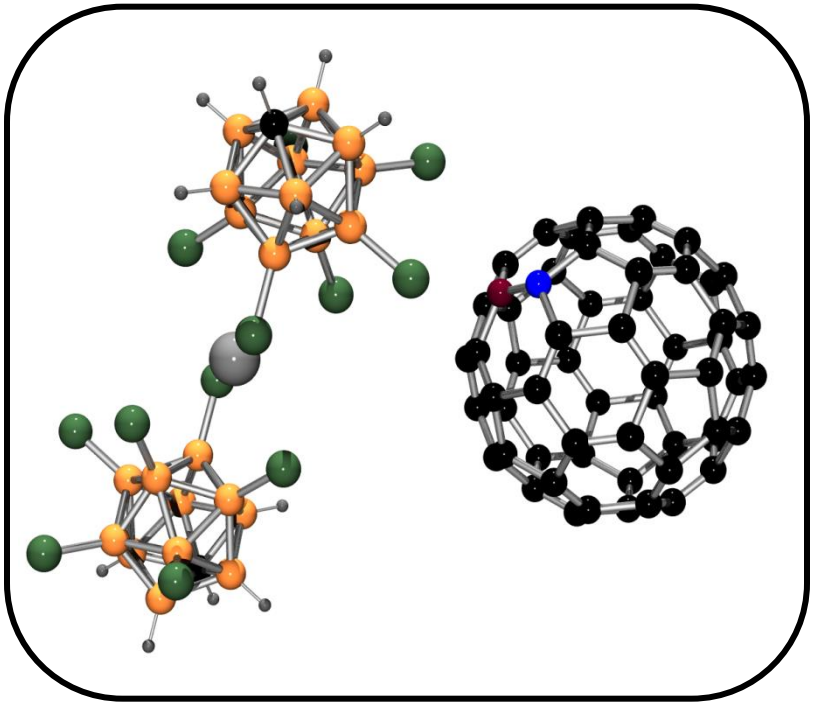
$\delta_{Corannulen}$ = 7.82 ppm

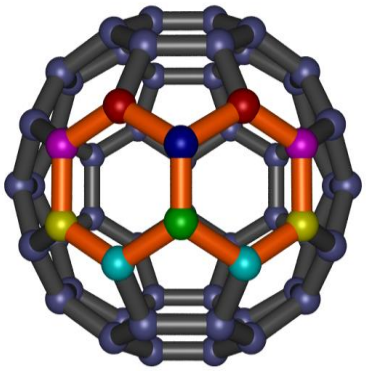


Fullerenes

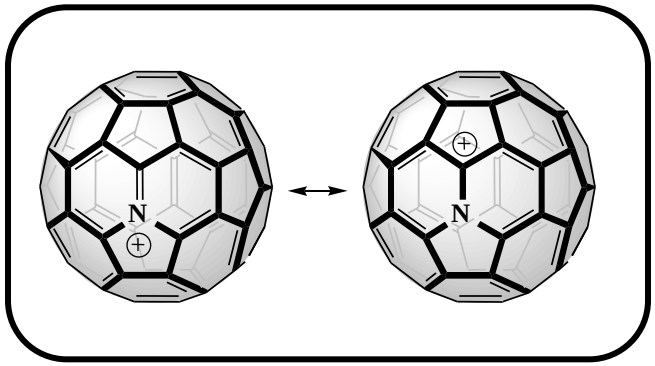
$C_{59}N^+$ - A key intermediate for azaheterofullerene functionalization:





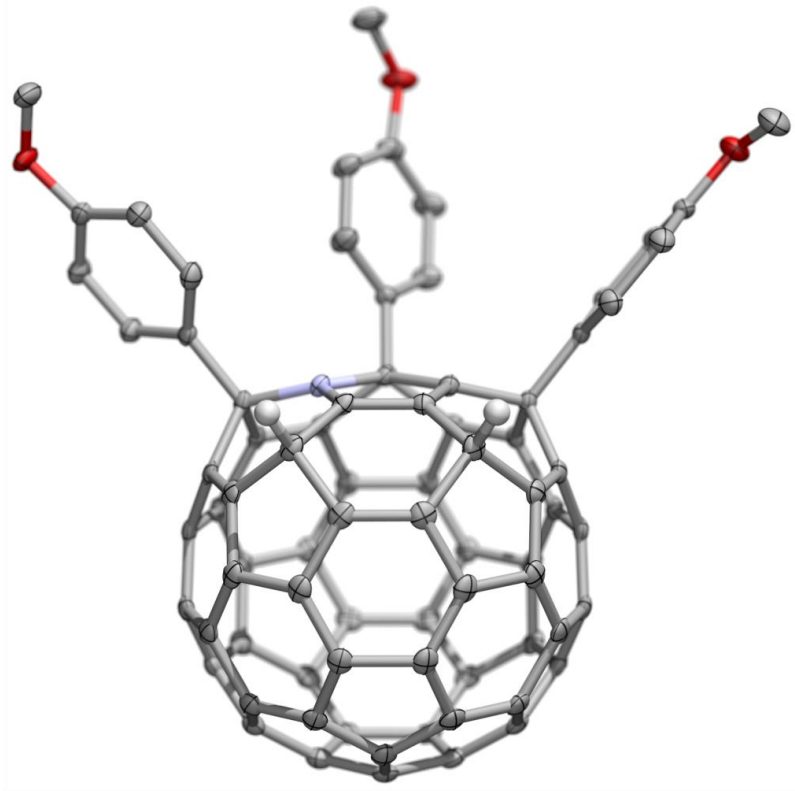


	MULLIKEN-Partialladung
	N
	0.050
	0.001
	0.079
	-0.047
	0.159

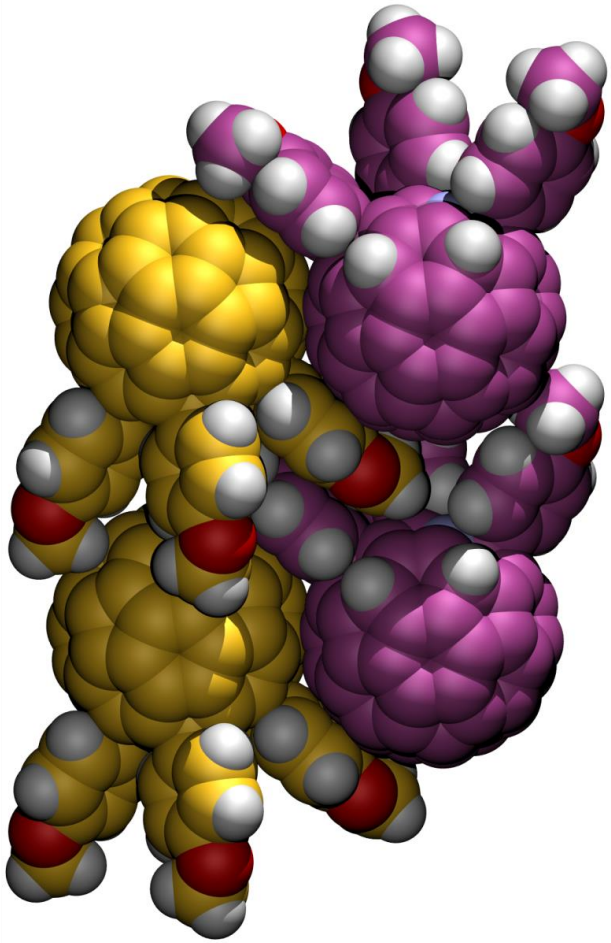


Heterofullerenes

a)

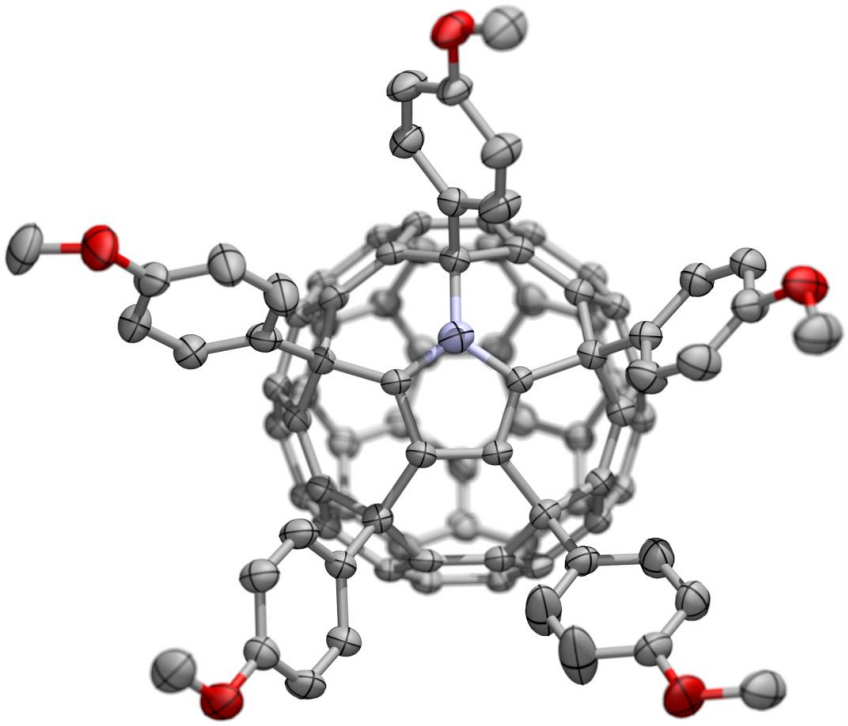


b)



Heterofullerenes

a)



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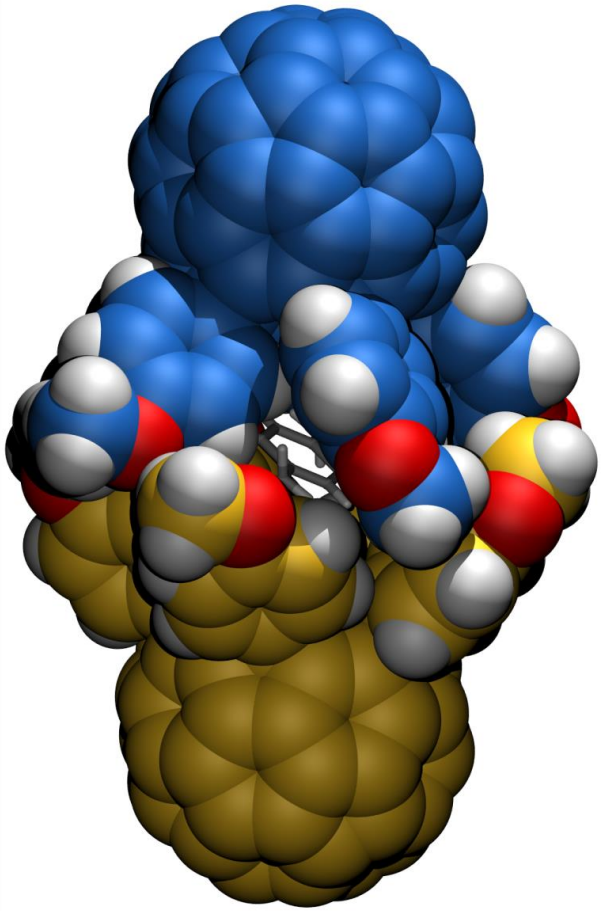
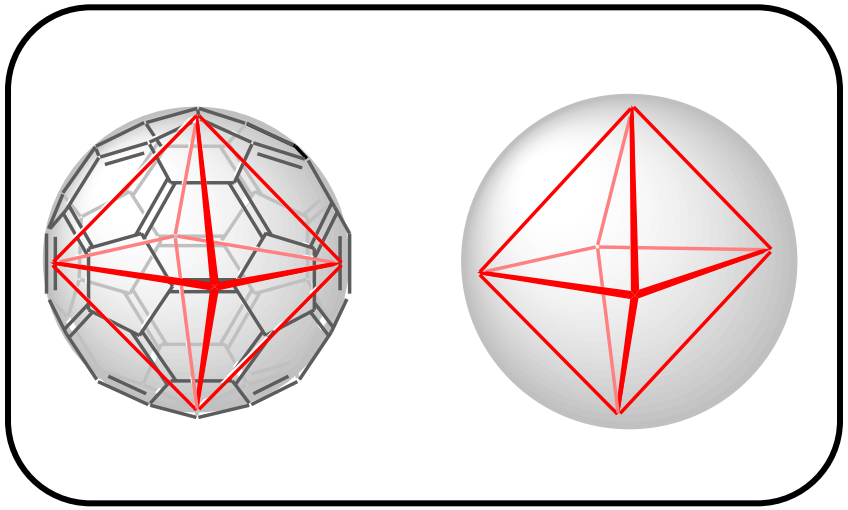
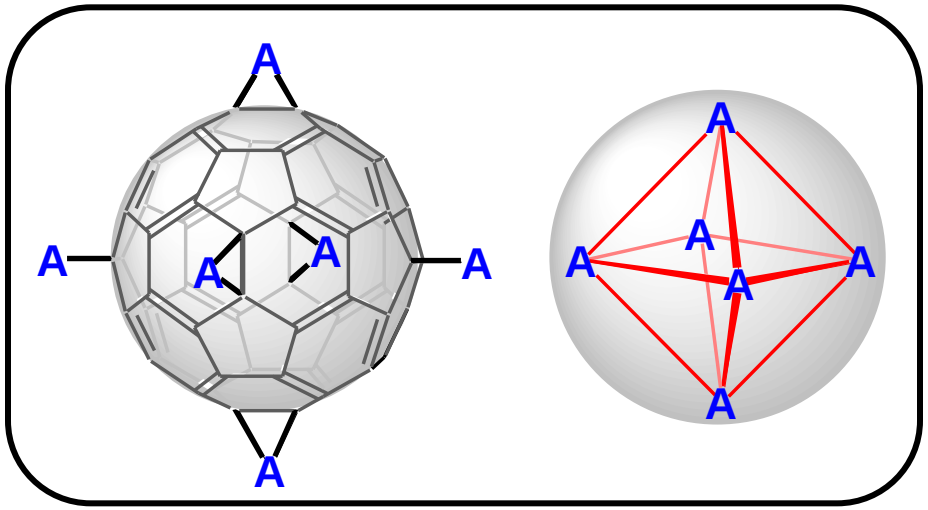


Fullerenes

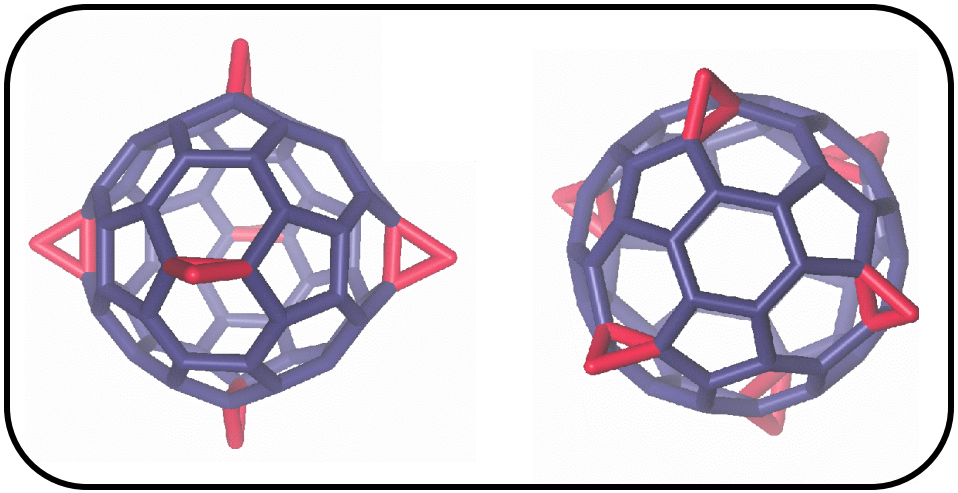




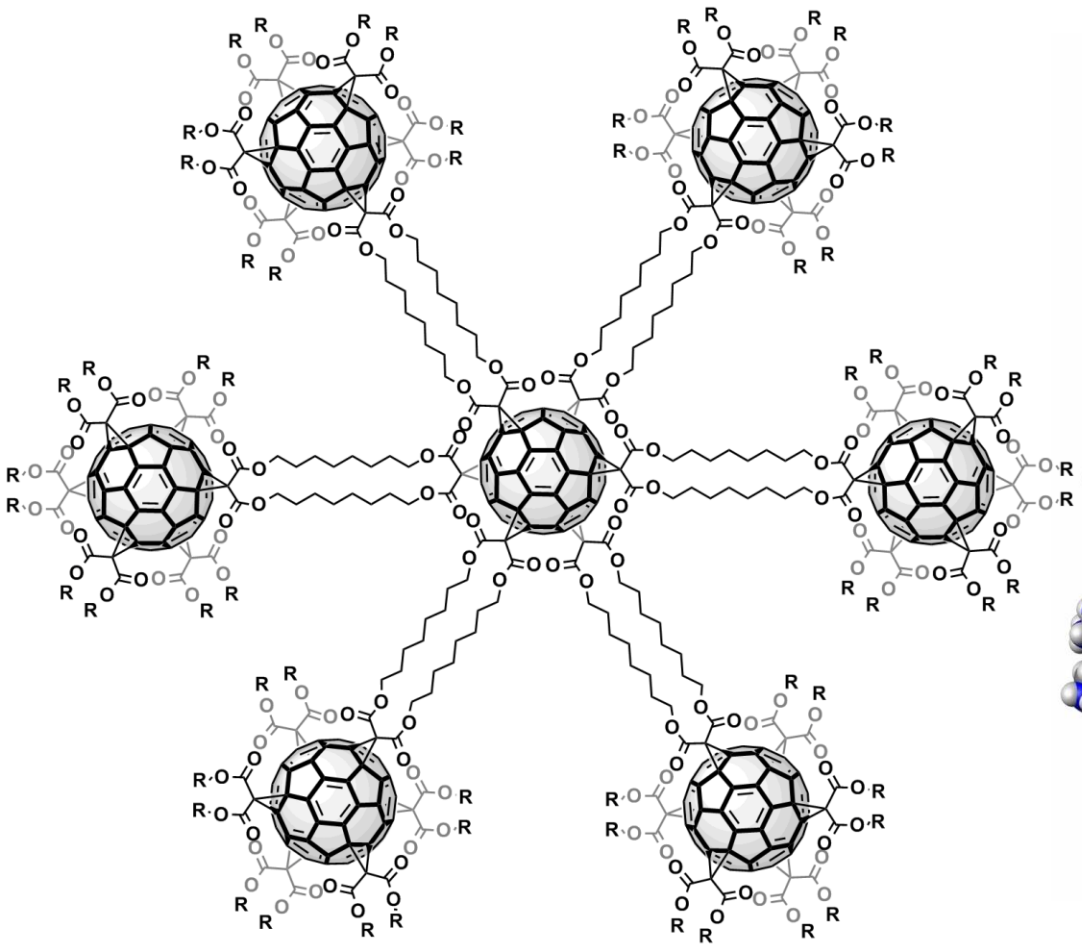
octahedral topology within C_{60}

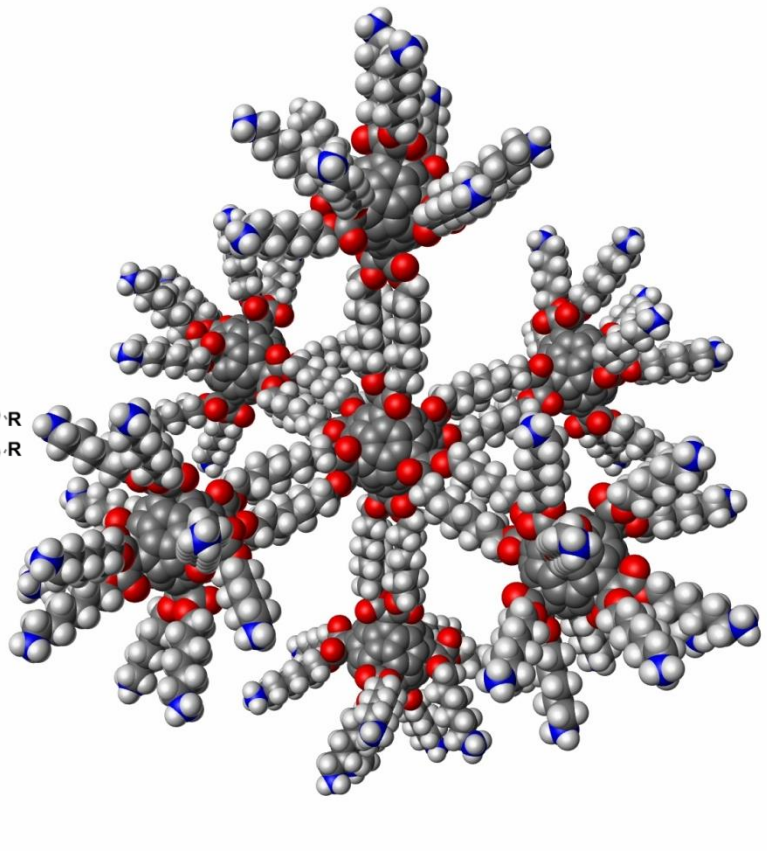
hexakisadduct

T_h symmetrical addition pattern

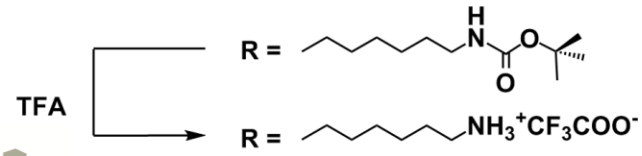


Globular Heptafullerenes

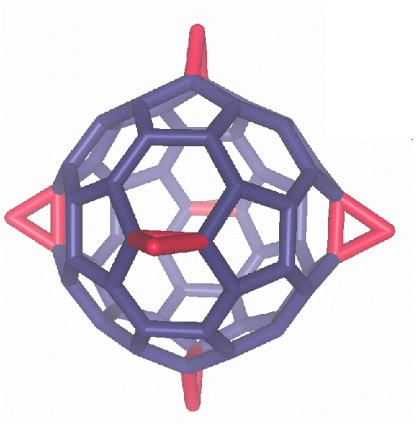


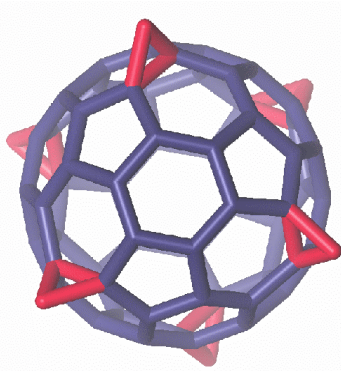


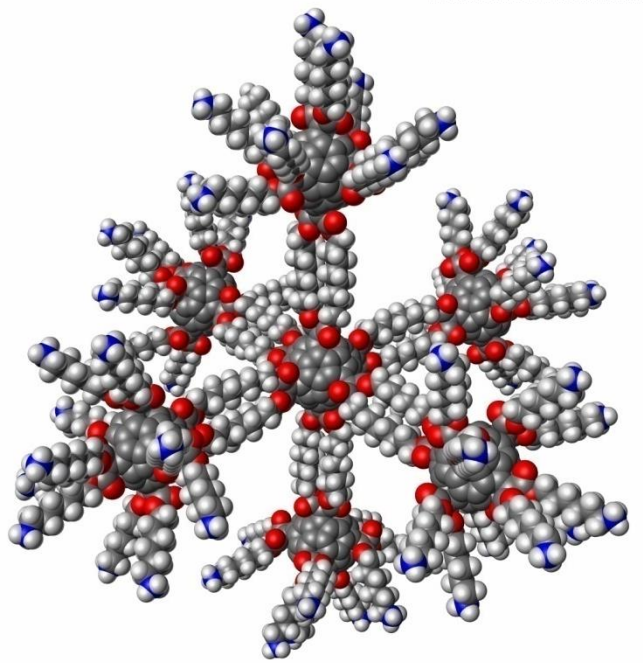
defined oligoelectrolyte with 60 positive charges!

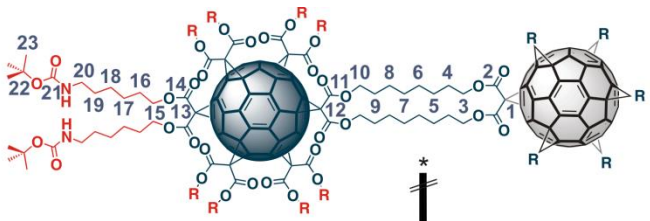


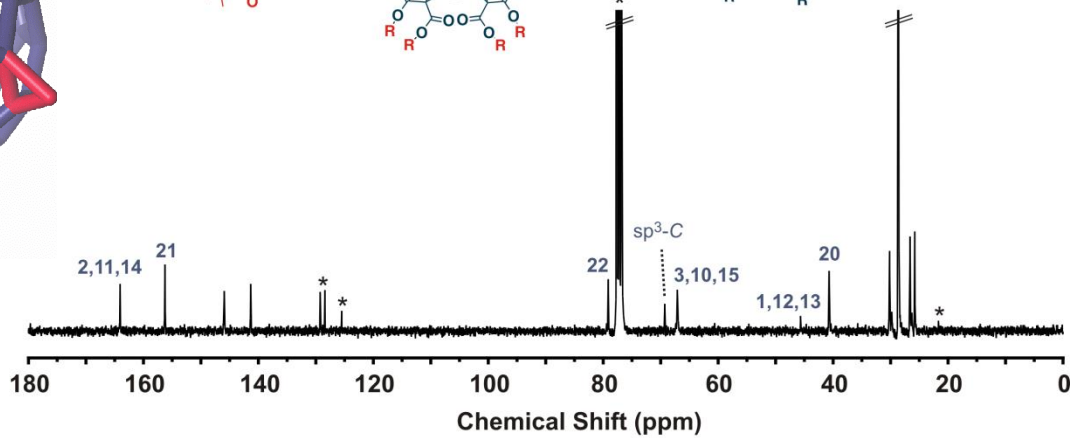
Globular Heptafullerenes

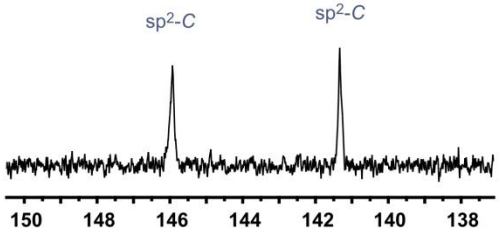


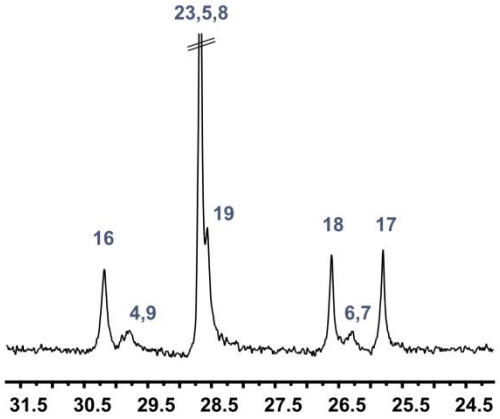




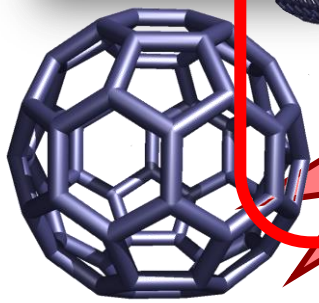




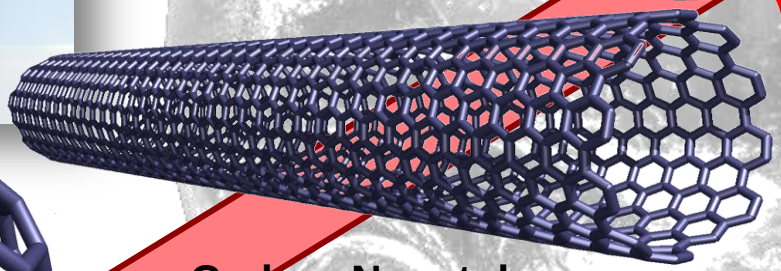




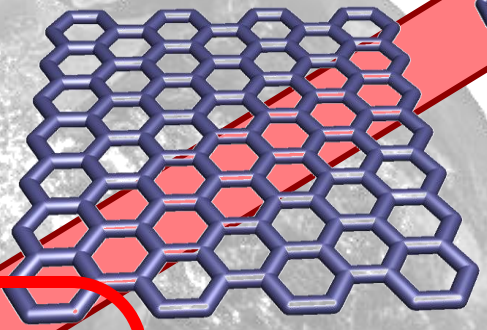
The World of Carbon



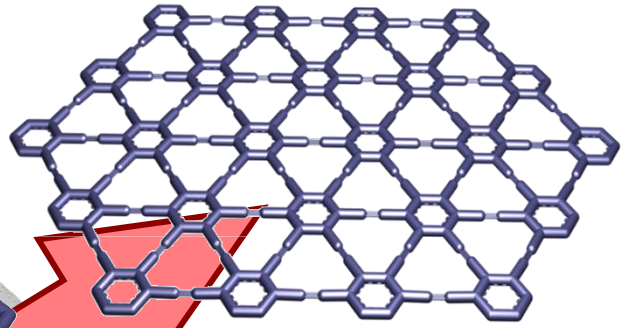
Fullerenes
1985



Carbon Nanotubes
1991



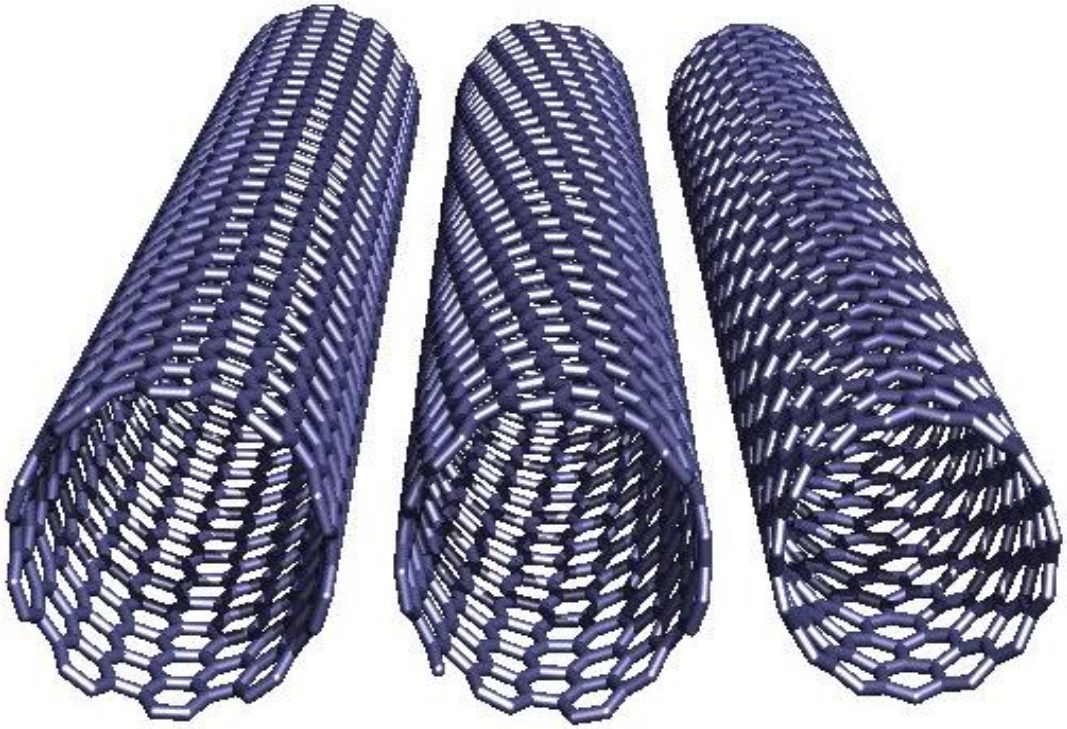
Graphene
2004



many undiscovered allotropes
e.g. sp-sp^2-Graphyne
> 20??

SCA
Synthetic Carbon Allotropes SFB953

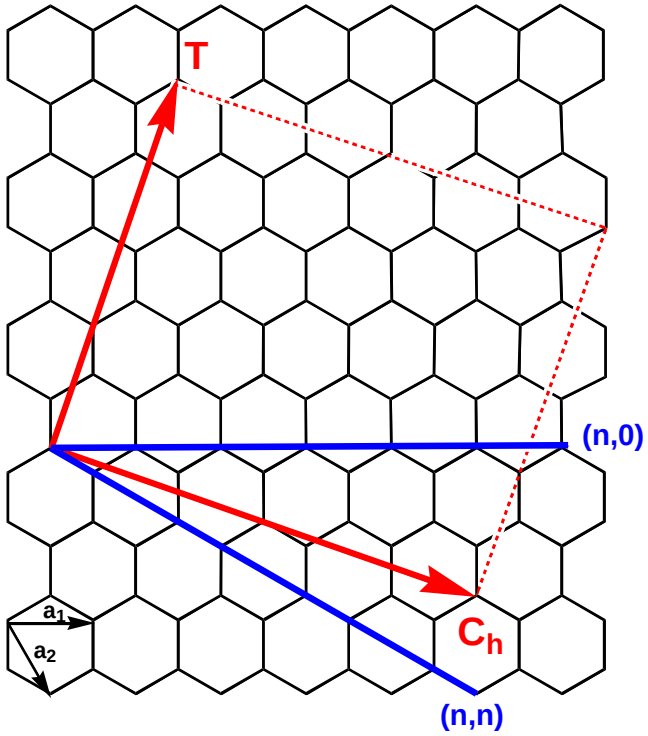
Carbon Nanotubes



(10,10)
metal

(12,7)
semiconductor

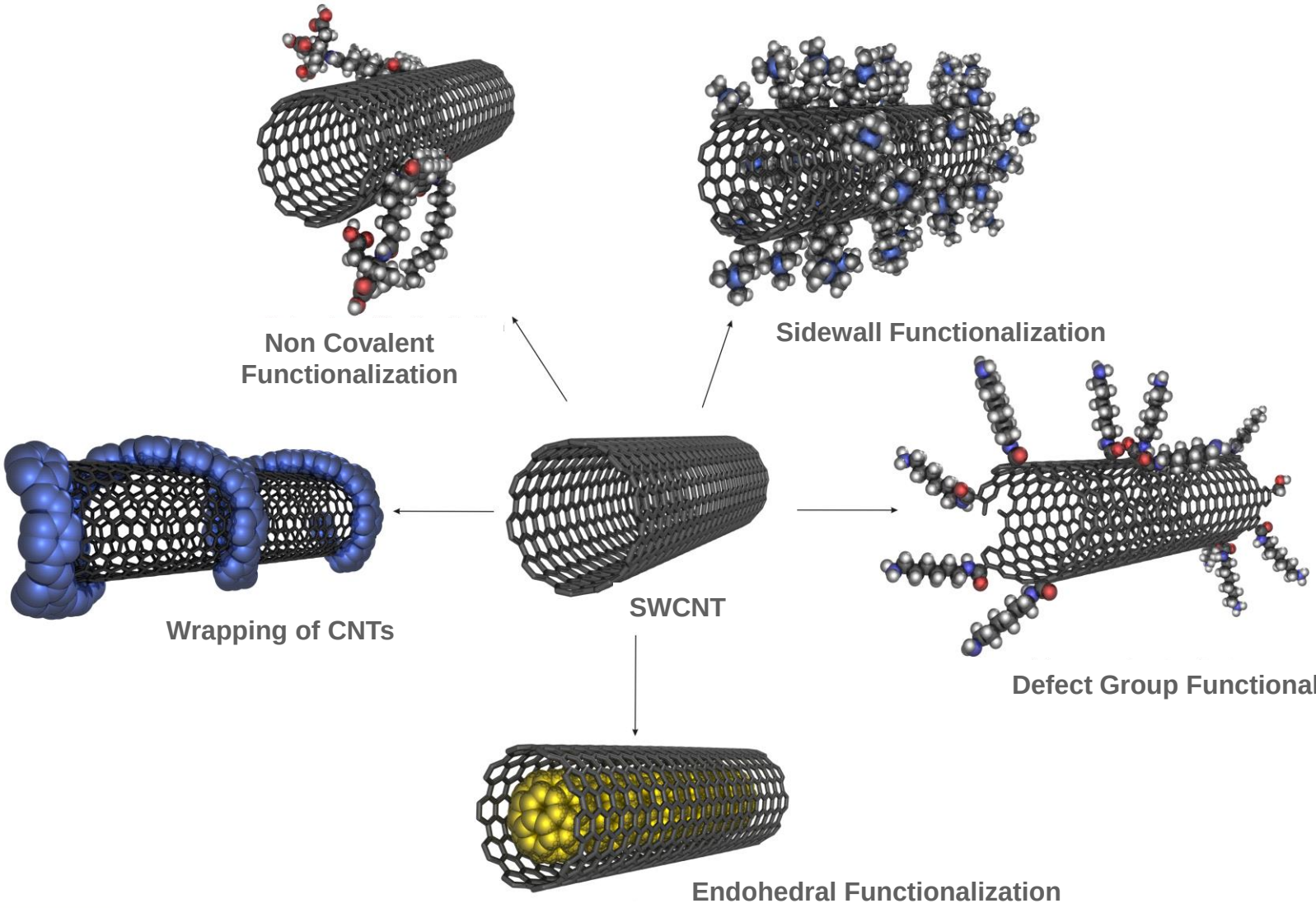
(15,0)
metal



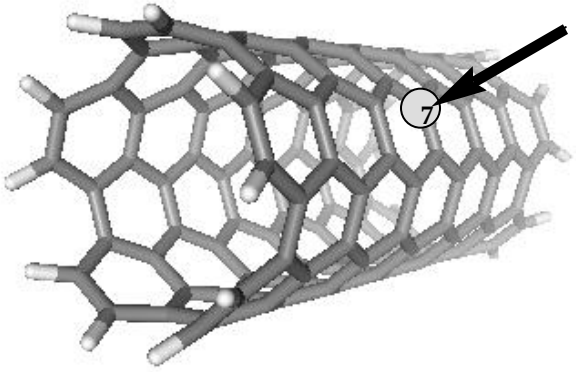
$C_h = na_1 + ma_2$

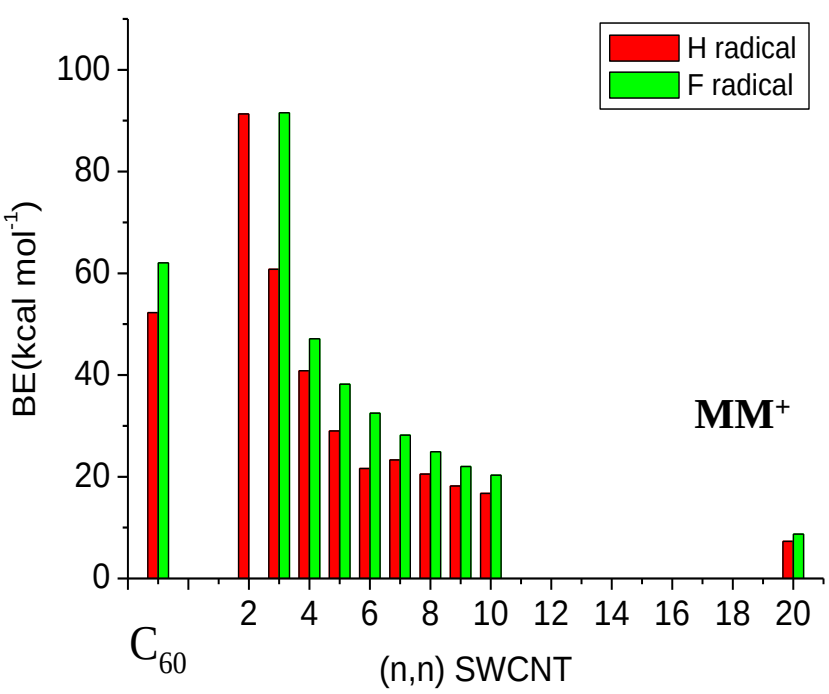
metal: (n-m)/3 = whole number

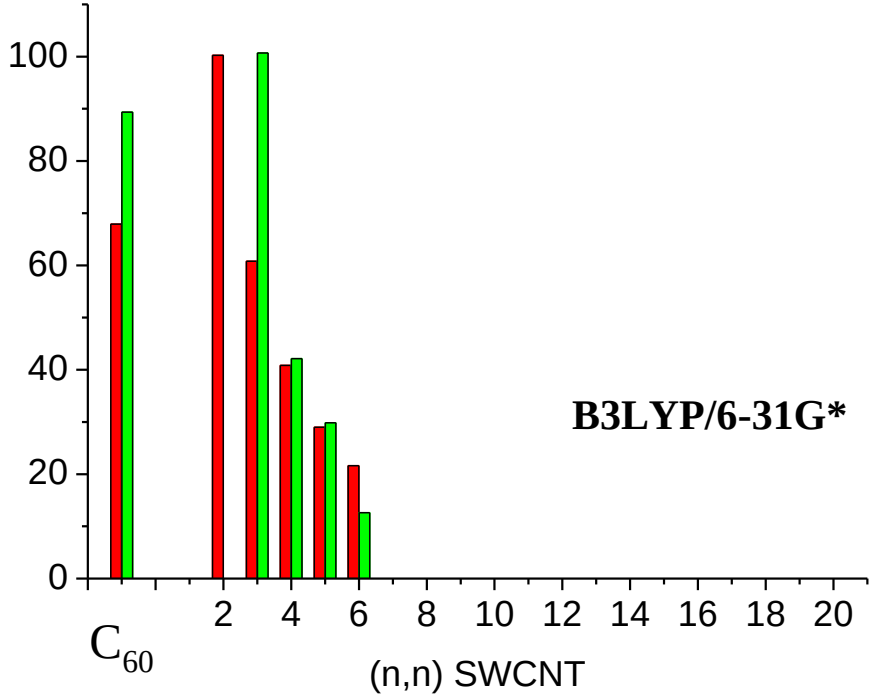
CNT-Functionalization



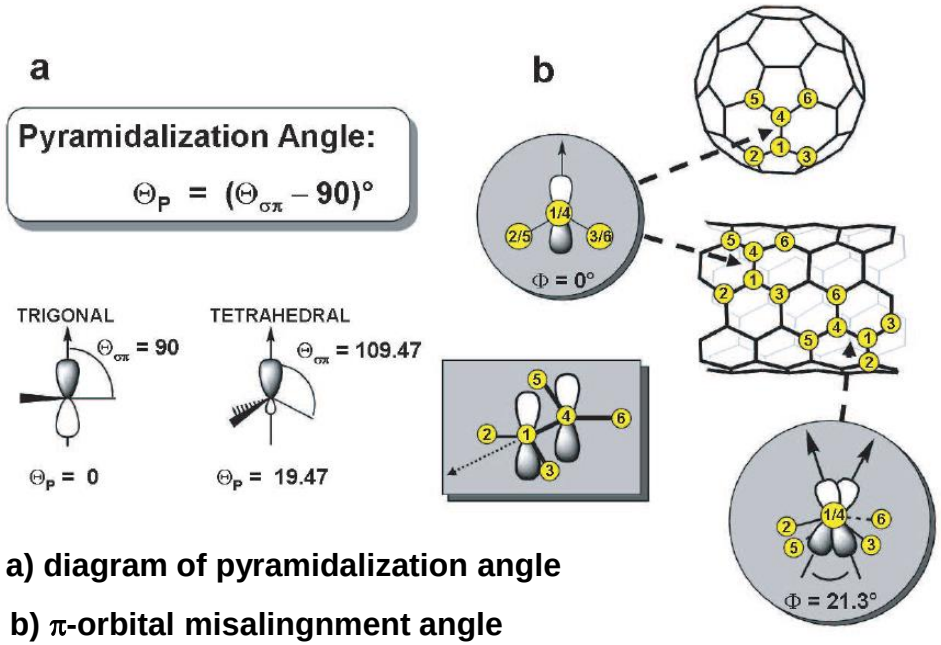
Side Wall Reactivity







Side Wall Reactivity

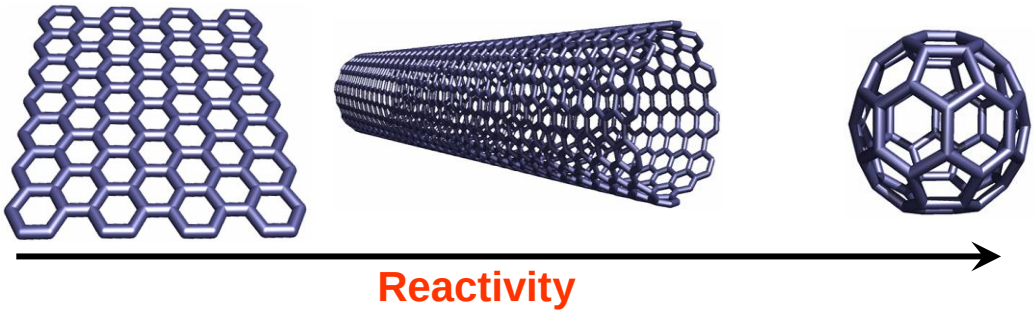


a) diagram of pyramidalization angle

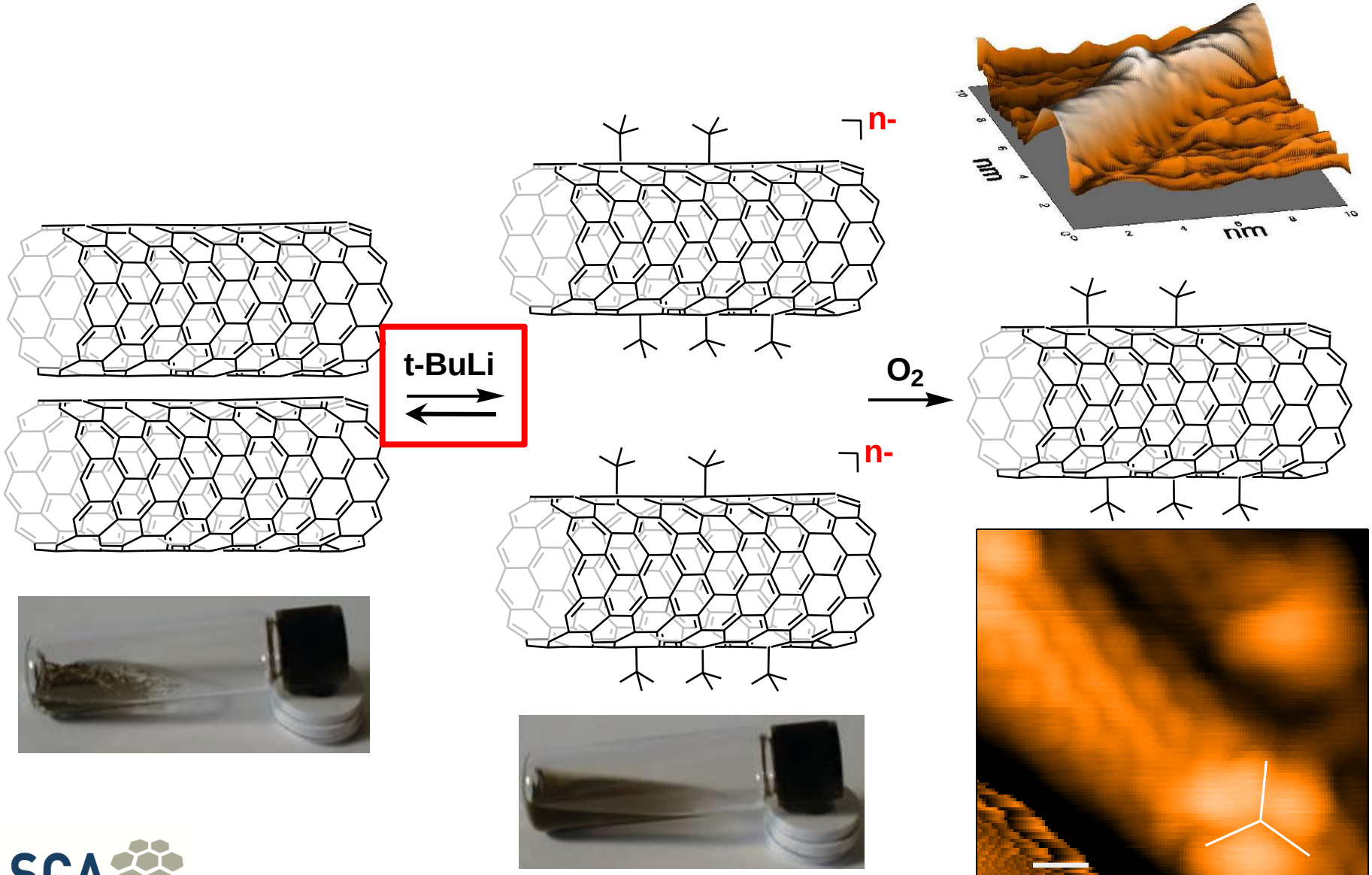
b) π-orbital misalingnment angle

- the diameter of a (5,5) tube (6.7 Å) can be compared to the the diameter of C_{60} (7.1 Å)
- CNT sidewalls are bent in 1D in contrast to the 2D curvature of C_{60}
  - (5,5): $\Theta_p = 6.0°$
    C_{60}: $\Theta_p = 11.6°$
- Only the smallest (and probably unstable) (2,2) (2.75 Å) tube has a higher pyramidalization angle than C_{60}

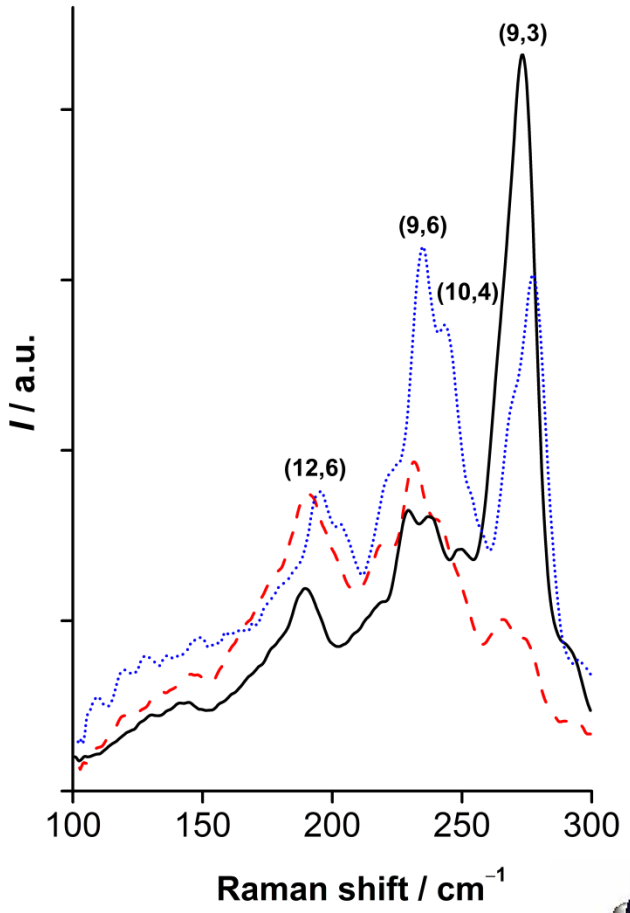
→ end cap reactivity is higher than side wall reactivity!!!

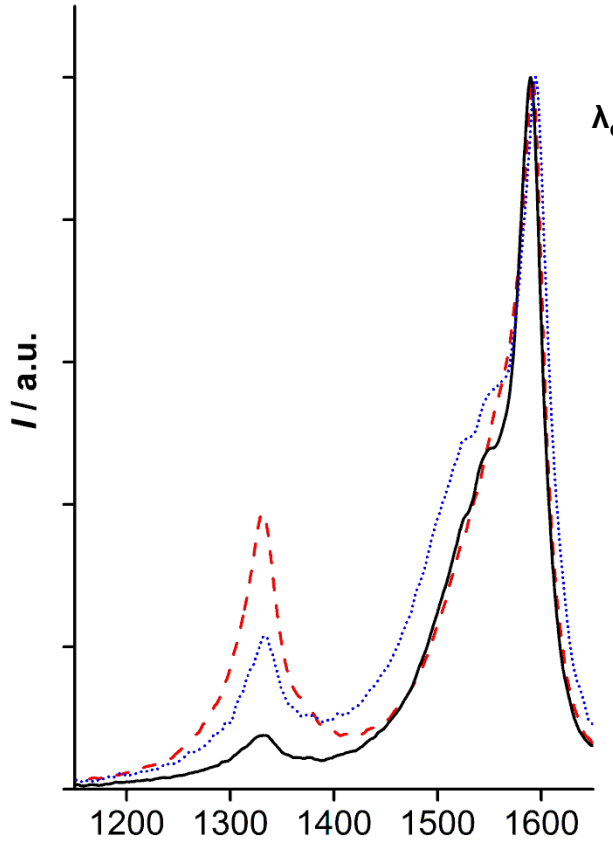


Alkylation of SWNTs



Selectivity

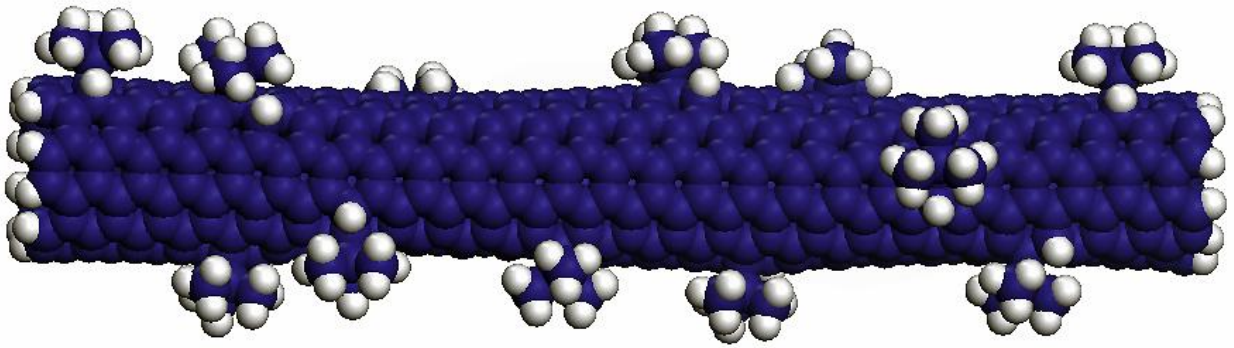




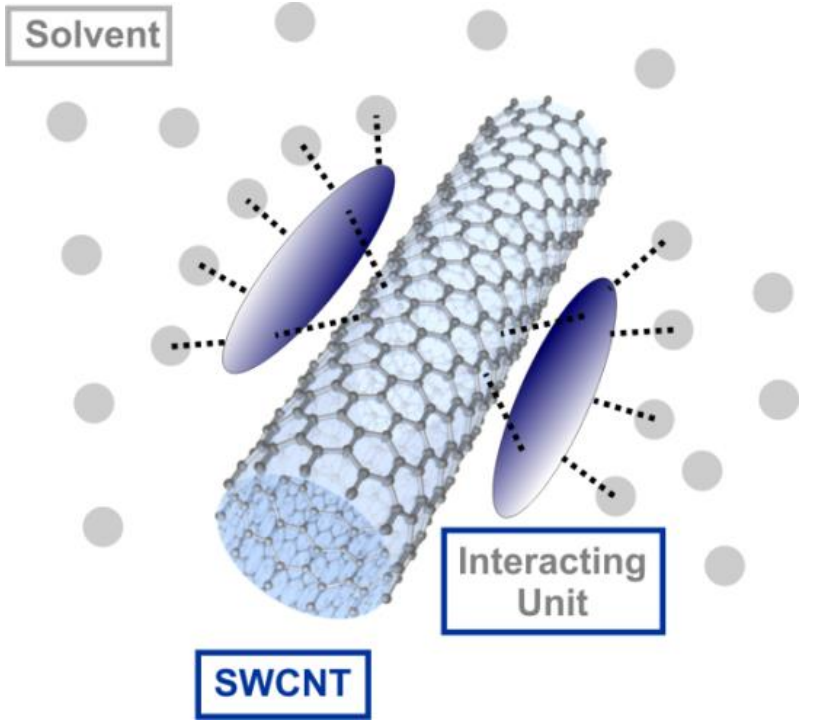
λ_{ex}= 532 nm (metallic)

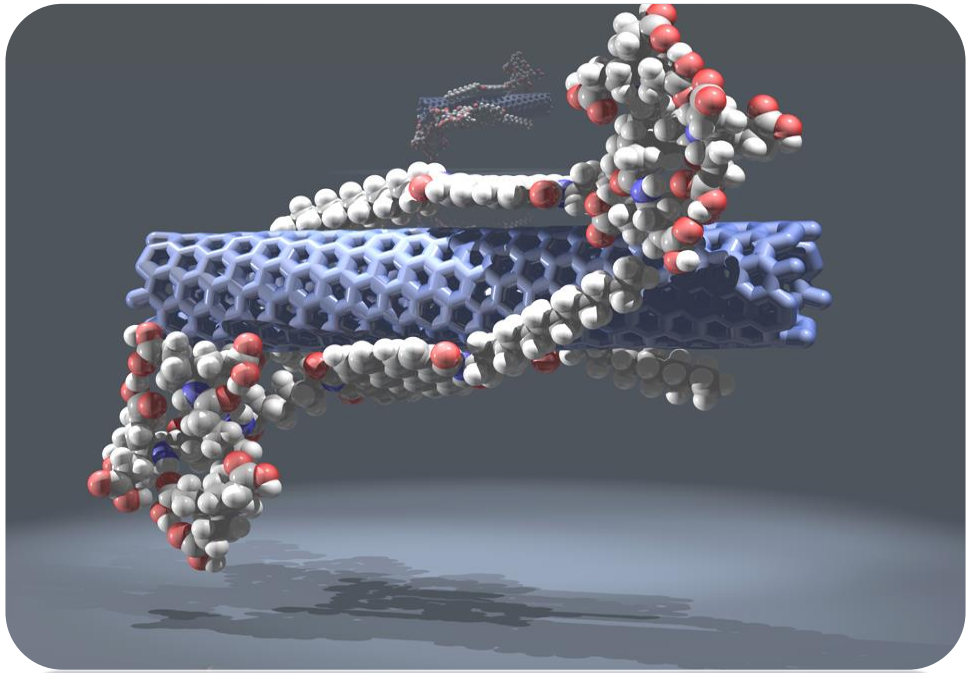
pristine SWNTs
***n*-Bu-SWNTs (*n*-BuLi)**
***t*-Bu-SWNTs (*t*-BuLi)**

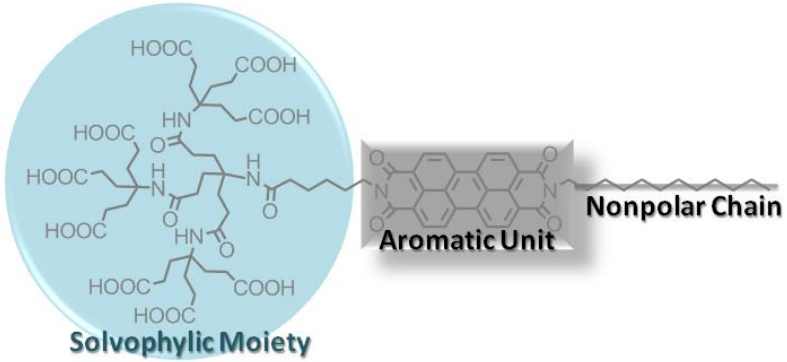
- reactivity inversely proportional to diameter

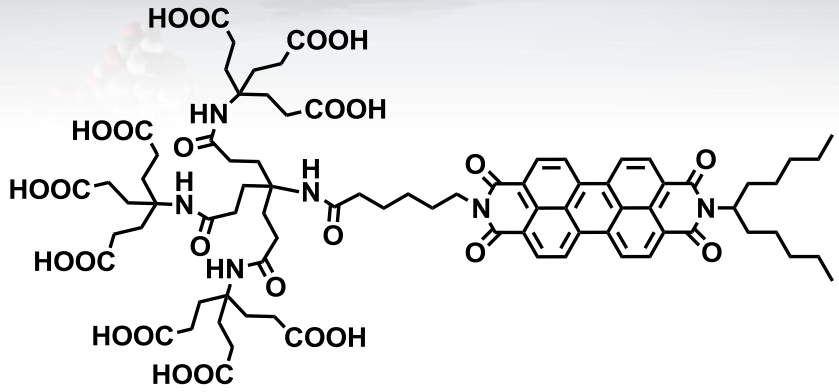


Noncovalent Functionalization





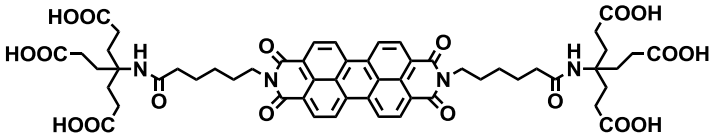




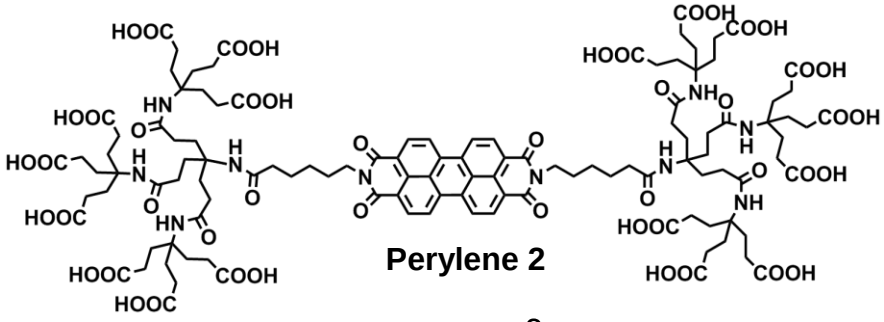
SCA
Synthetic Carbon Allotropes SFB953

Dispersion Behavior

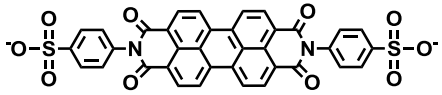
Bolaamphiphilic Perylenes



Perylene 1 [1]

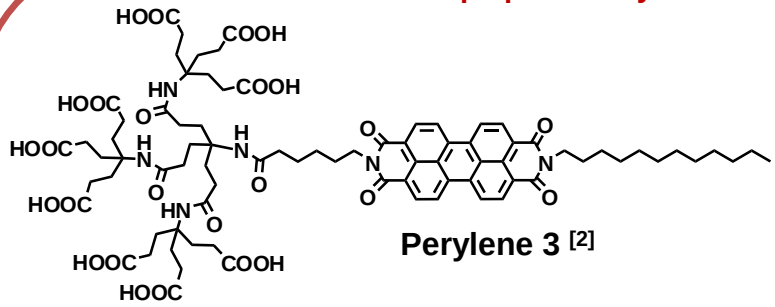


Perylene 2

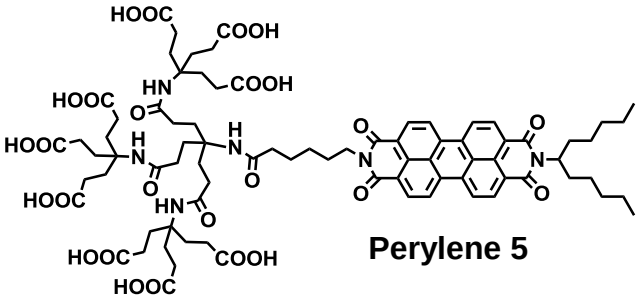


Perylene 4

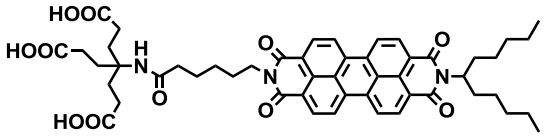
Amphiphilic Perylenes



Perylene 3 [2]

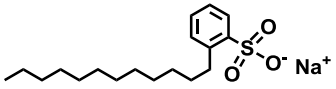


Perylene 5

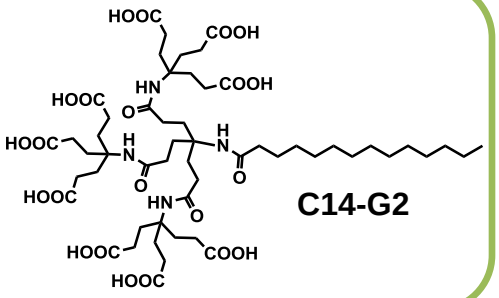


Perylene 6

Other Amphiphiles

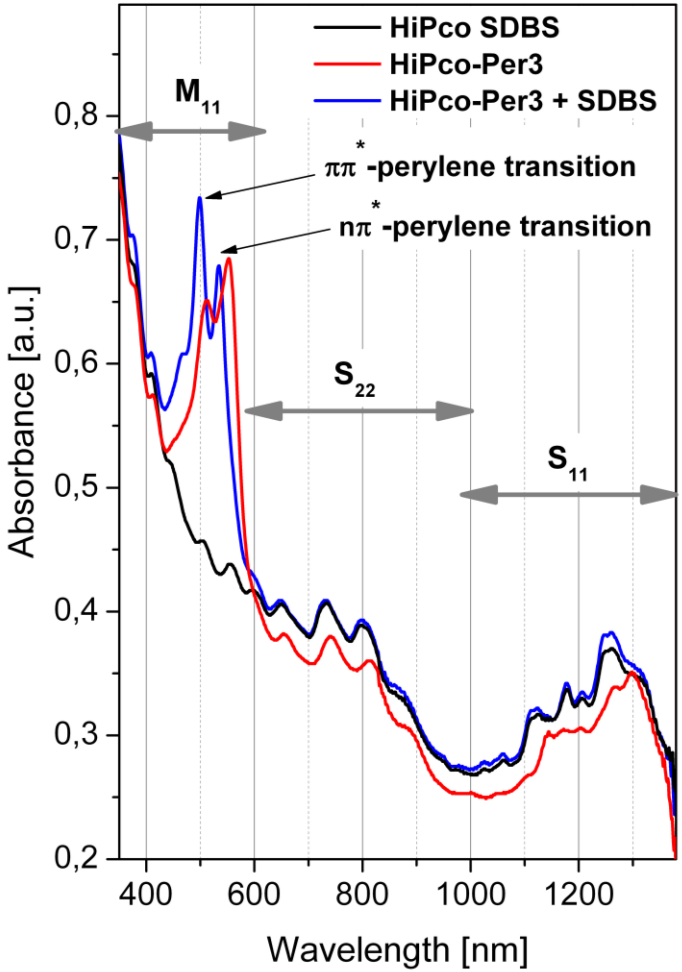


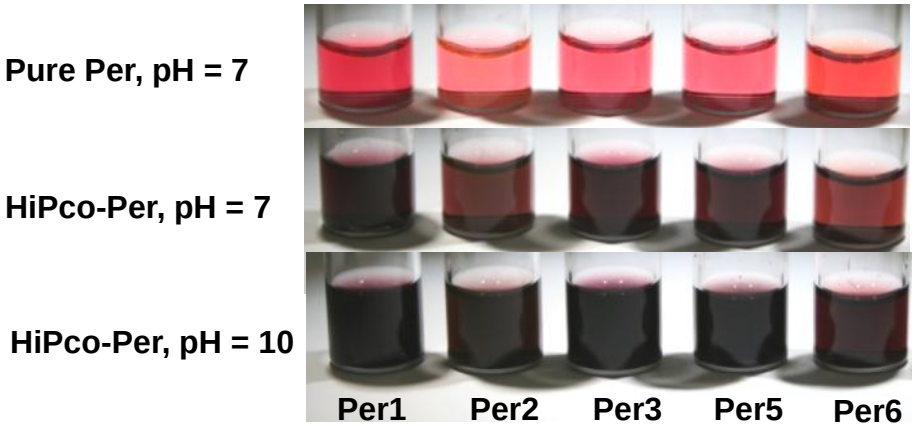
SDBS



C14-G2

Dispersion Behavior

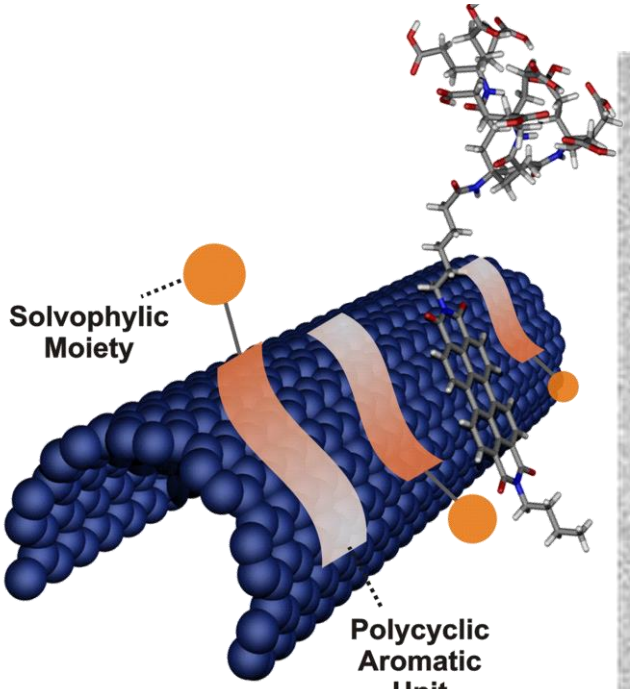


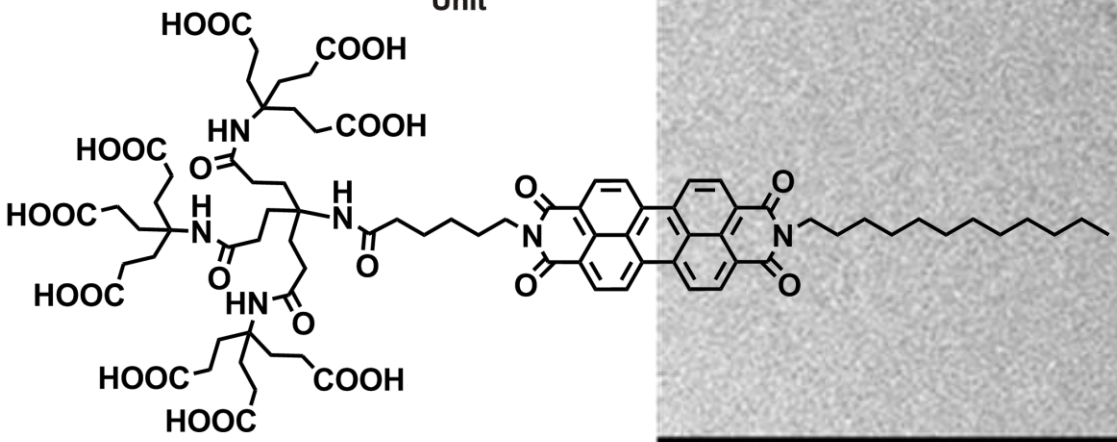


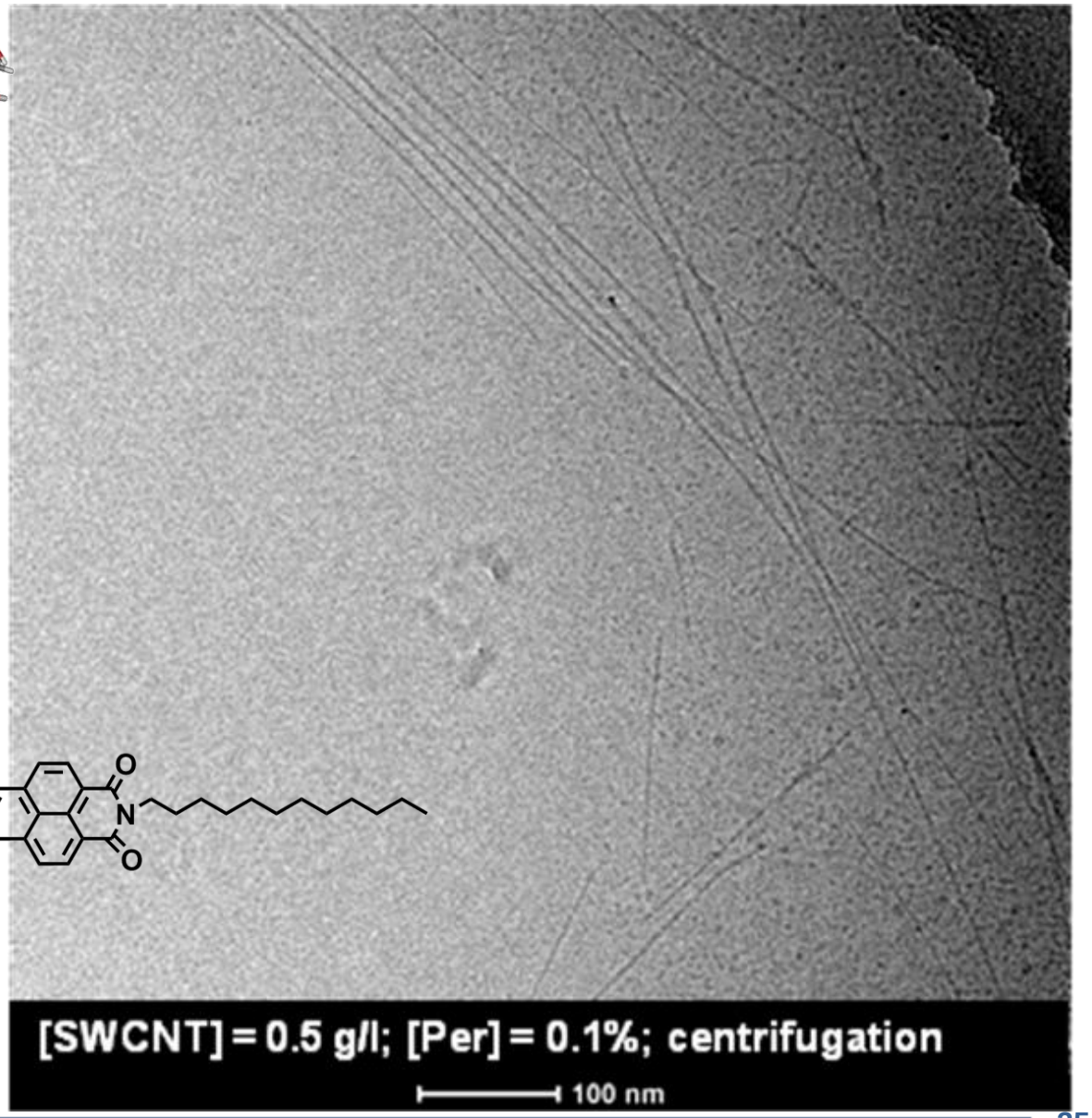
- **Red-shift of CNT spectral absorption features (vHS) compared to SDBS except for Per6 → micellar adsorption**
- **Larger amount of nanotubes stably dispersed after centrifugation for pH = 10 compared to pH = 7**

	Per1 (0.1g/l)	Per2 (0.1g/l)	Per3 (0.1g/l)	Per5 (0.1g/l)	Per6 (0.1g/l)	SDBS (0.1g/)	SDBS (10g/l)
pH = 7	33 %	23 %	34 %	31 %	18 %	Not. Det.	68 %
pH = 10	66 %	39 %	**73 %**	**73 %**	33 %	Not. Det.	69 %

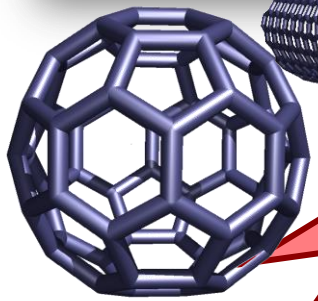
Cryo-TEM


Solvophylic
Moiety
Polycyclic
Aromatic
Unit

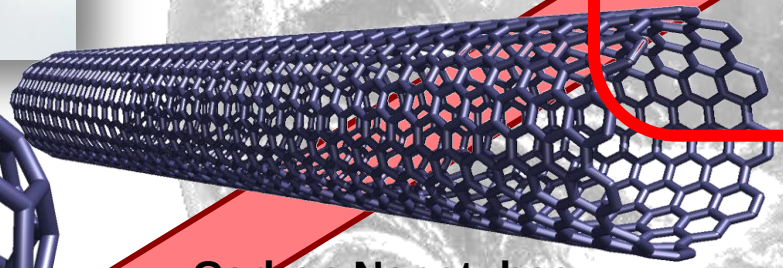

HOOC
COOH
HN
COOH
HOOC
O
HOOC
H
N
H
N
O
O
N
O
O
HOOC
HN
O
HOOC
COOH
HOOC


[SWCNT] = 0.5 g/l; [Per] = 0.1%; centrifugation
100 nm

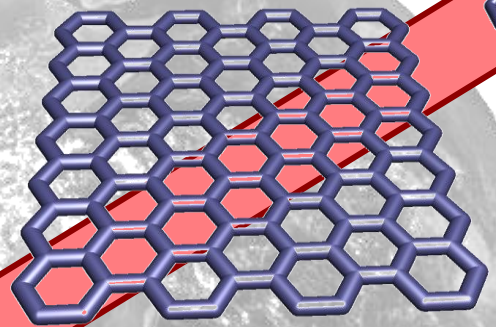
The World of Carbon



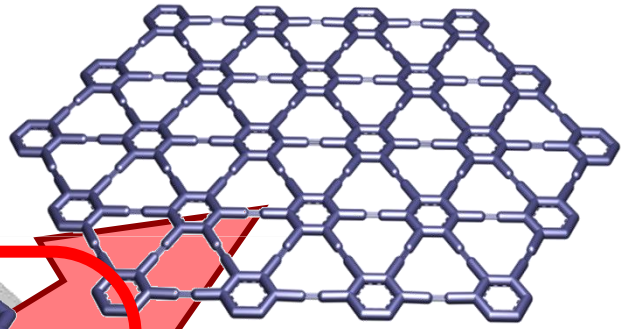
Fullerenes
1990



Carbon Nanotubes
1991



Graphene
2004

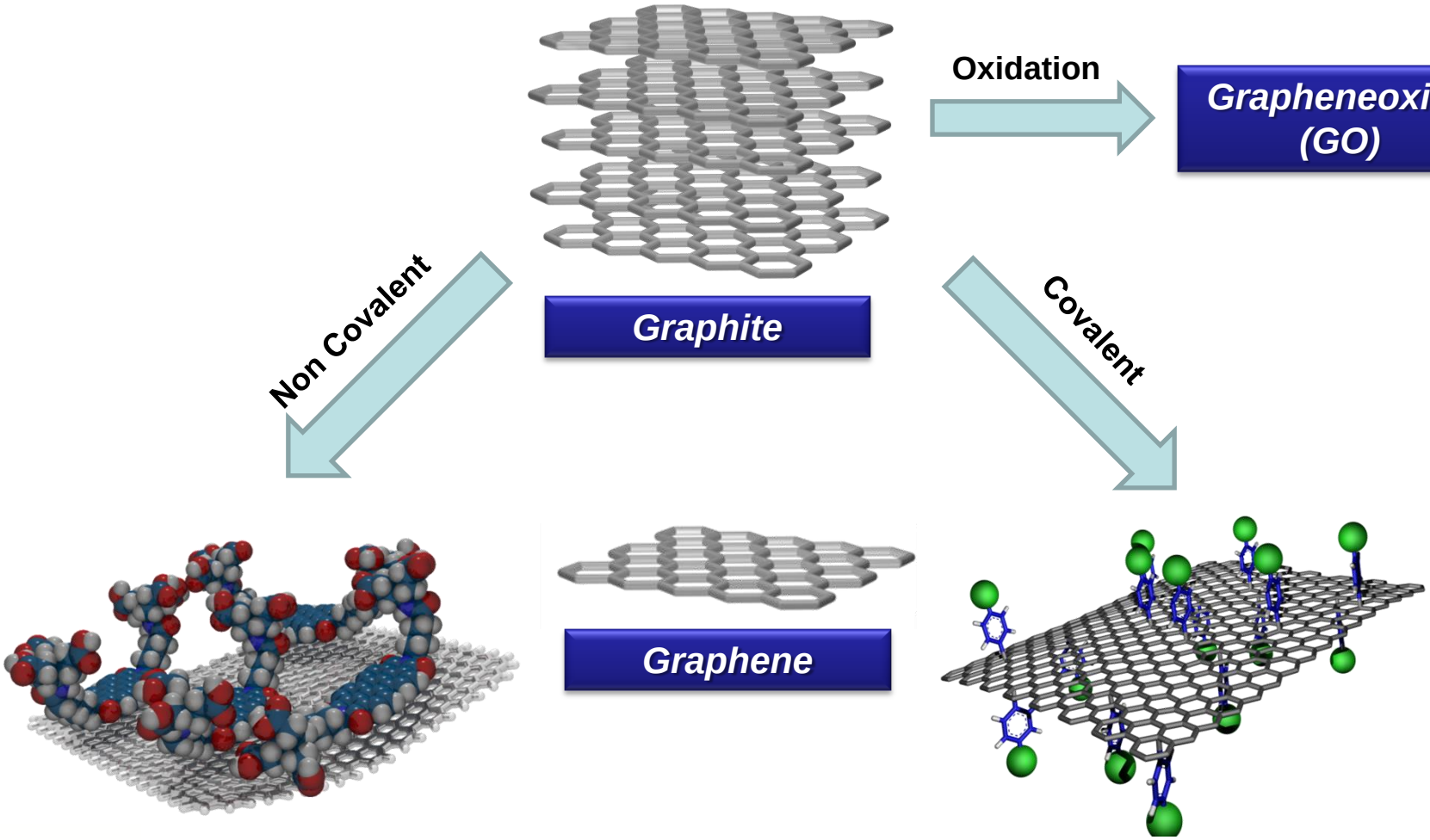


many undiscovered allotropes
e.g. sp-sp^2-Graphyne
> 20??

SCA
Synthetic Carbon Allotropes SFB953

Graphene Functionalization

The Top Down Approach



Starting with Graphene Models

COMMUNICATION www.rsc.org/chemcomm | ChemComm

Exfoliation of hexa-*peri*-hexabenzocoronene in water†‡

Jan M. Englert,[a] Frank Hauke,[a] Xingliang Feng,[b] Klaus Müllen[b] and Andreas Hirsch*[a]

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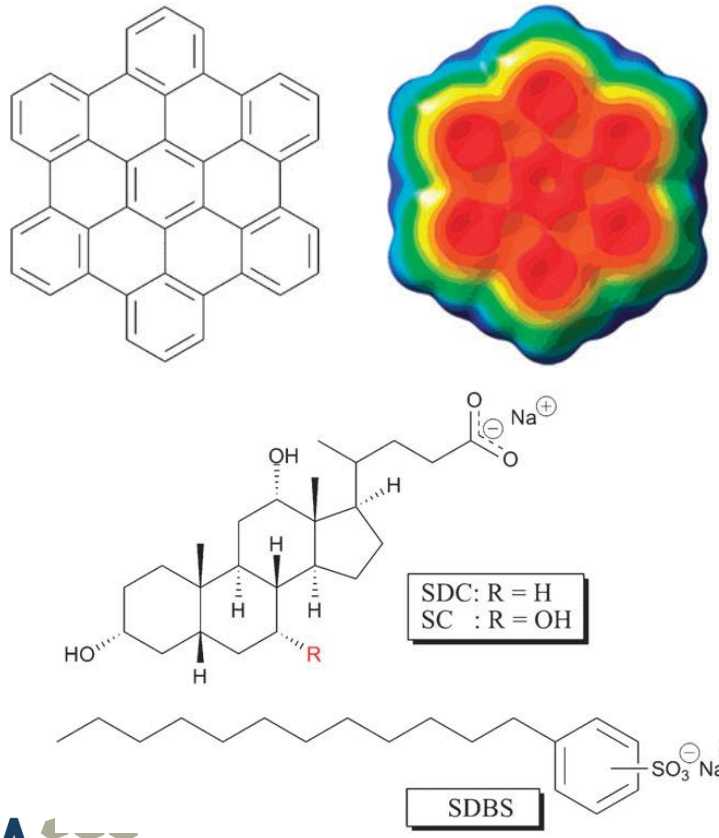
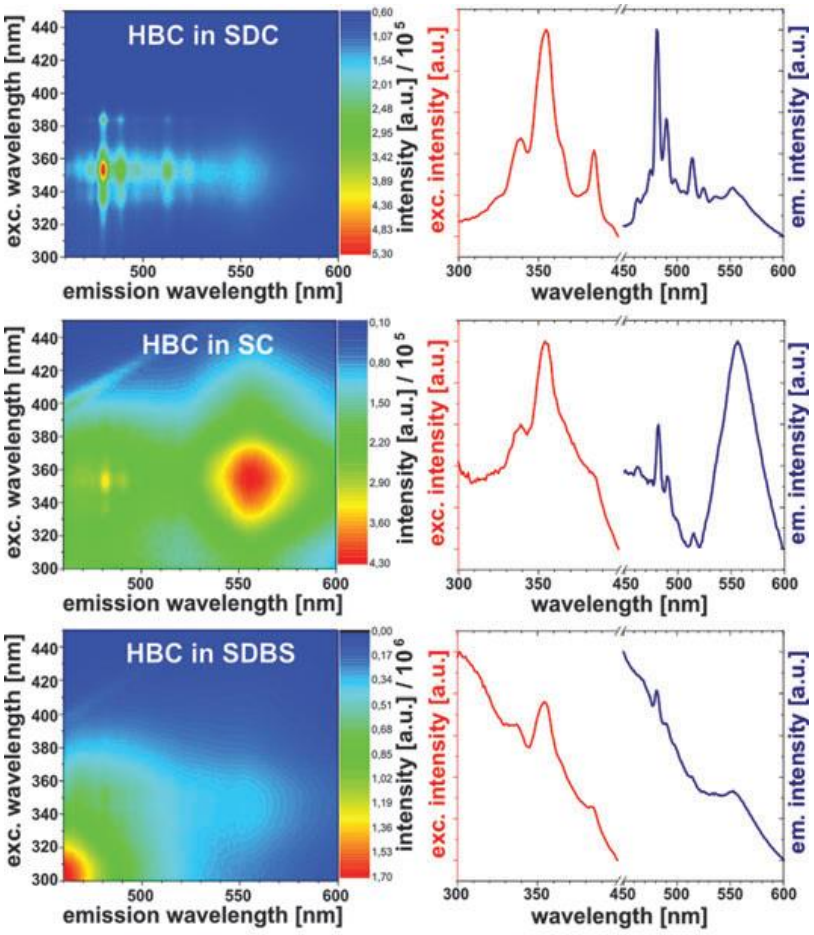
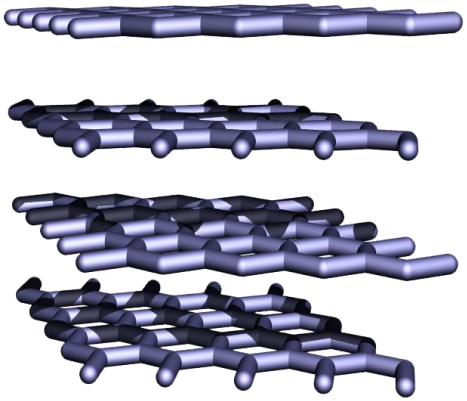
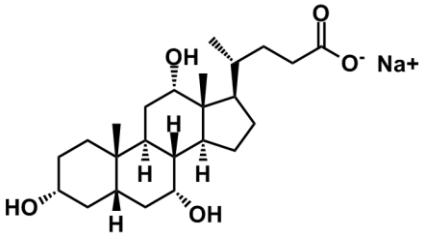
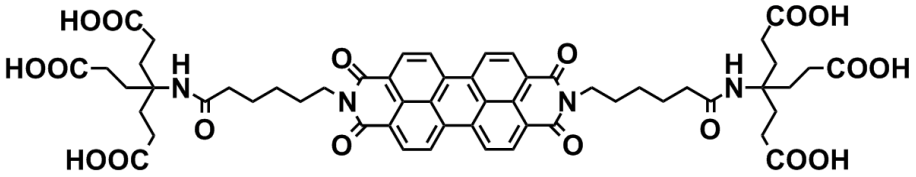




Dispersion in Water







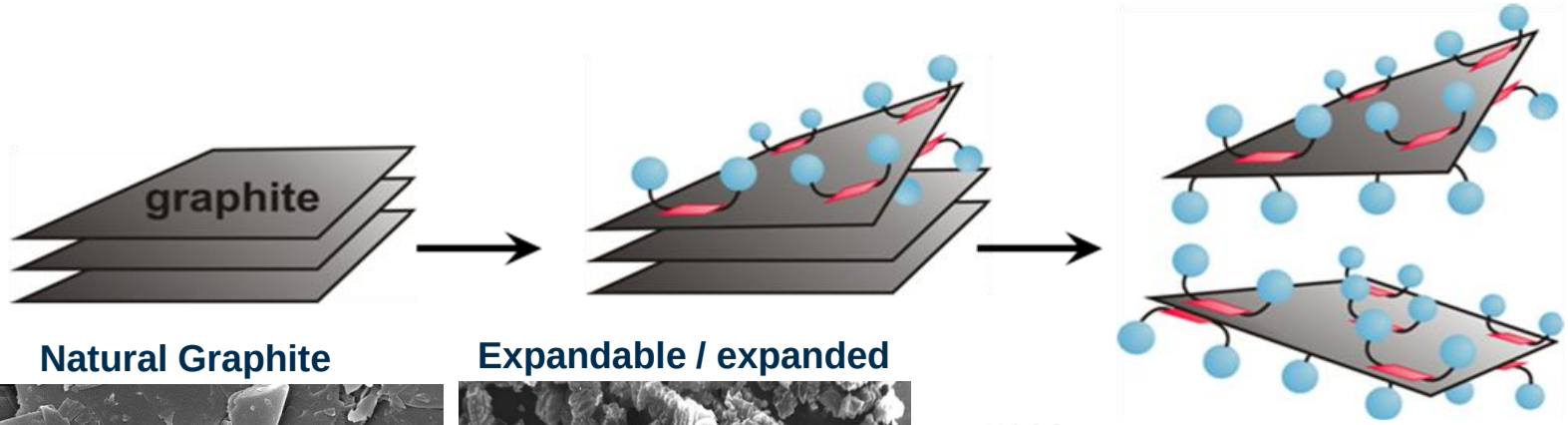
After ultrasonication

After centrifugation

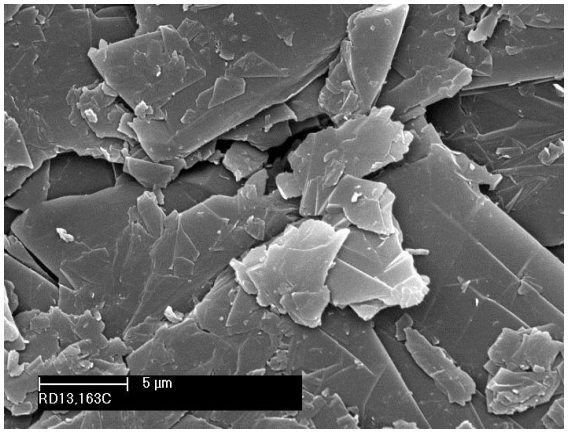
$C_{surf,\ sum} = 10^{-3}$ M

SC : Per = 1:1 mol

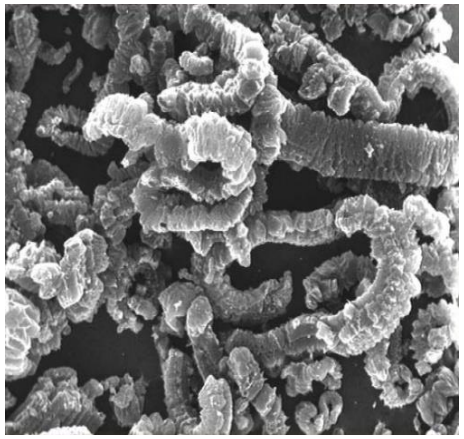
Dispersion in Water

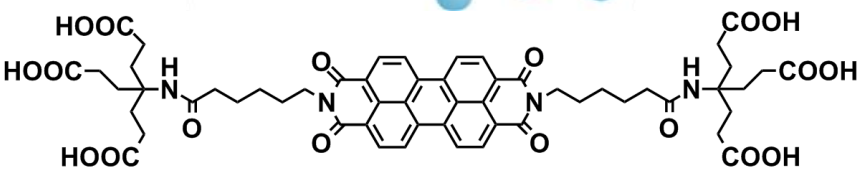


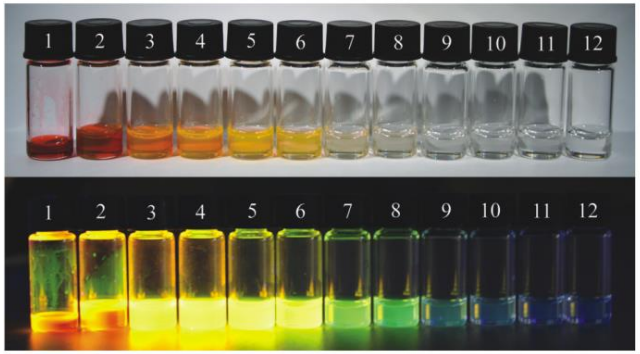
Natural Graphite

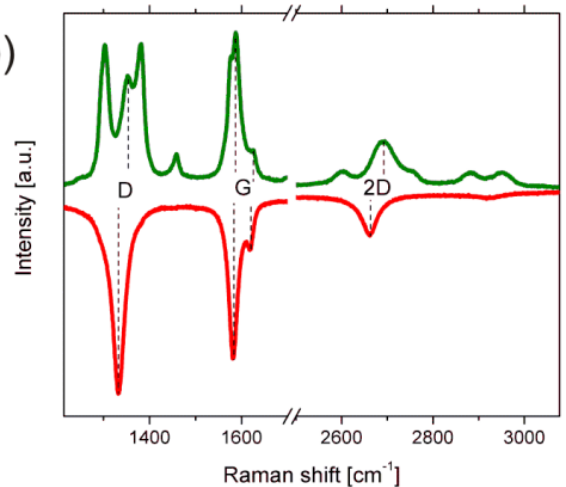


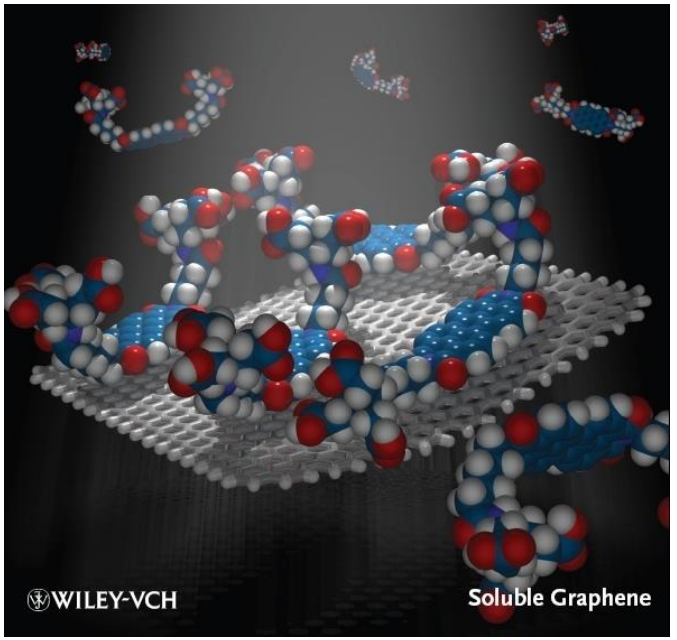
Expandable / expanded



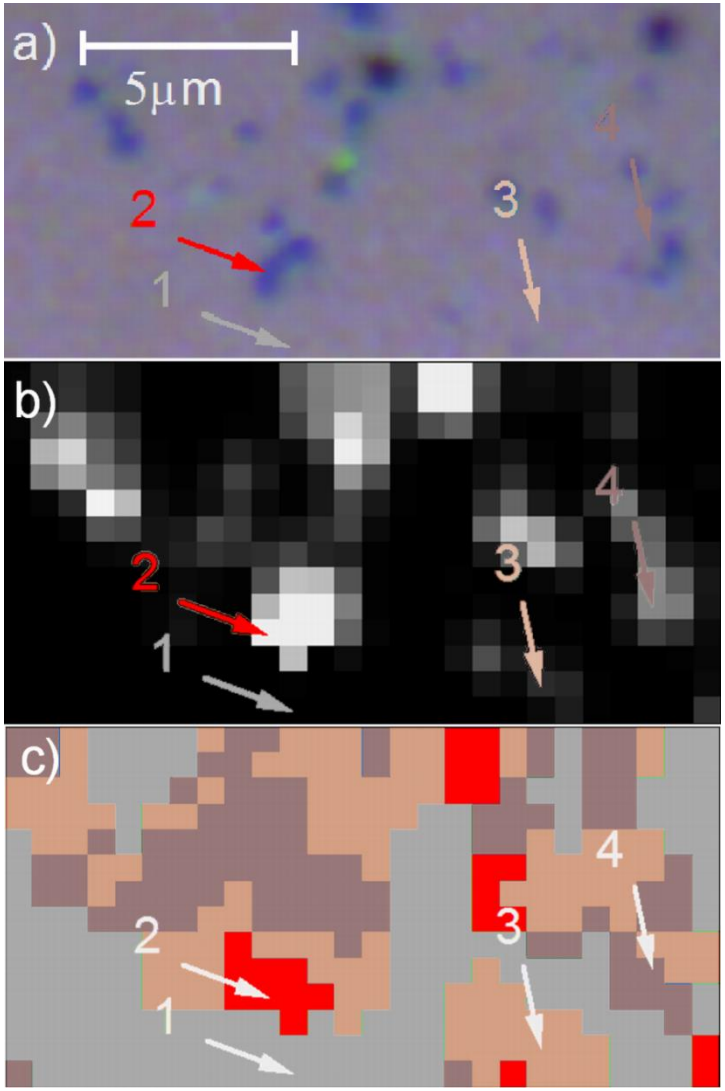


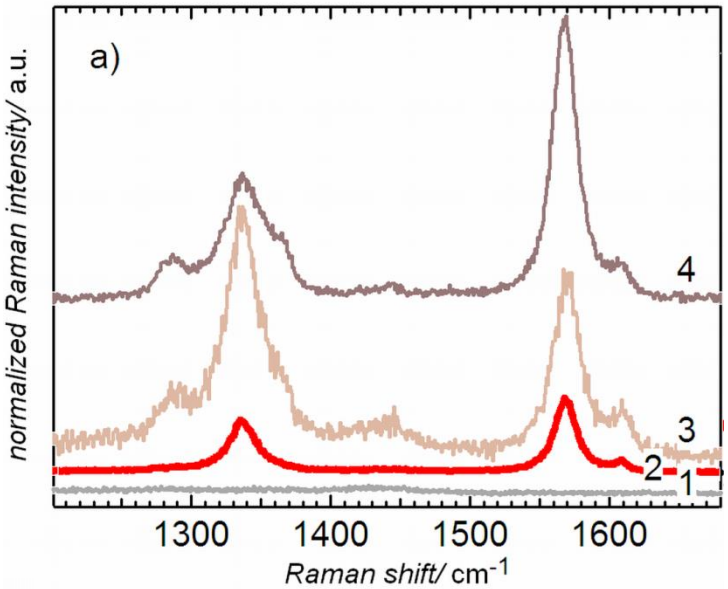


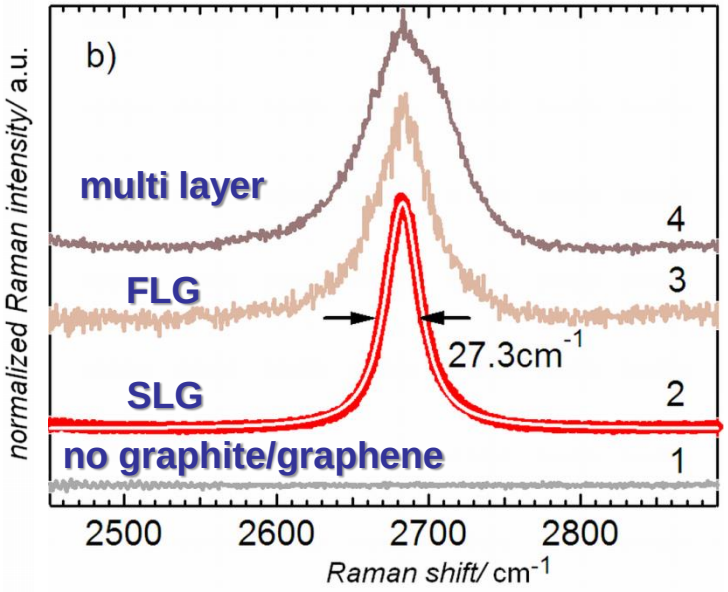




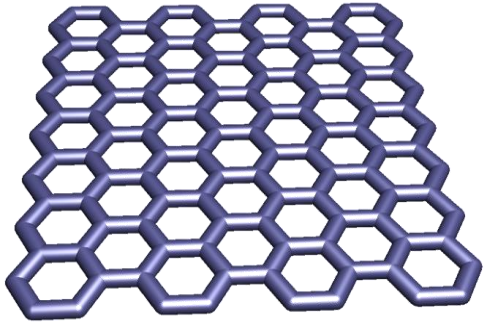
Deposition on Si/SiO_2

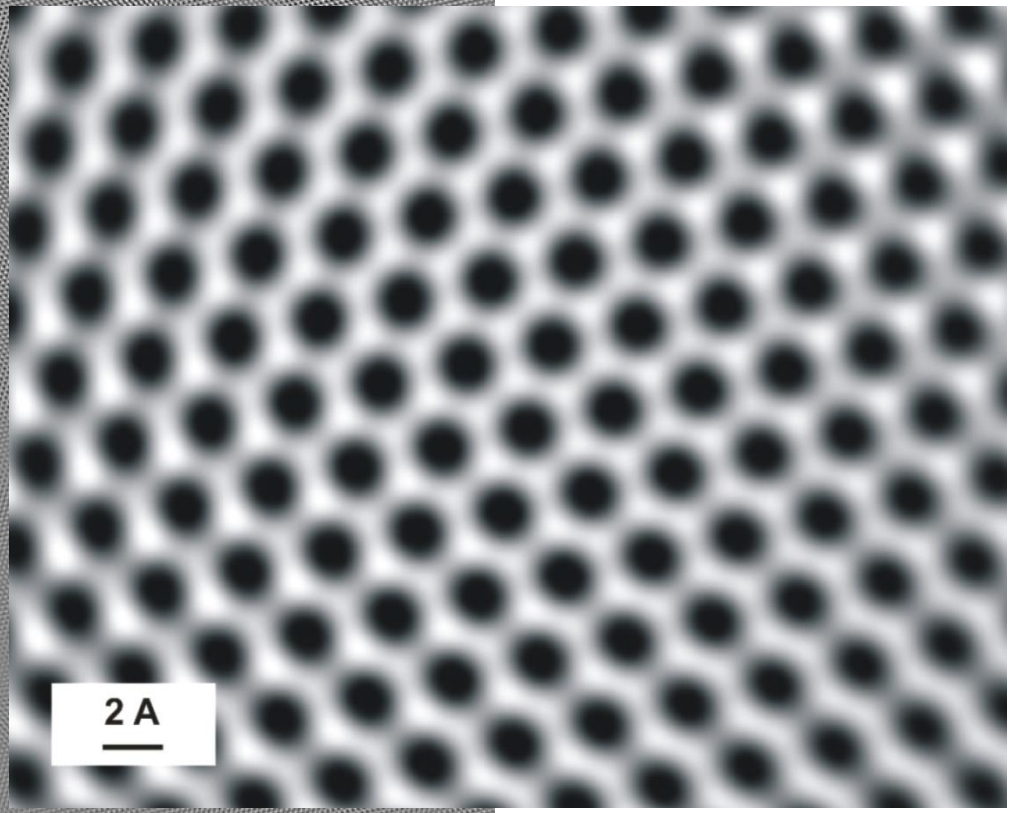






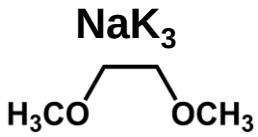
Deposition on Si/SiO_2

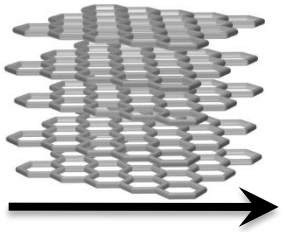


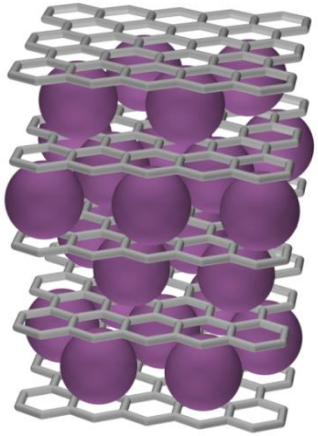


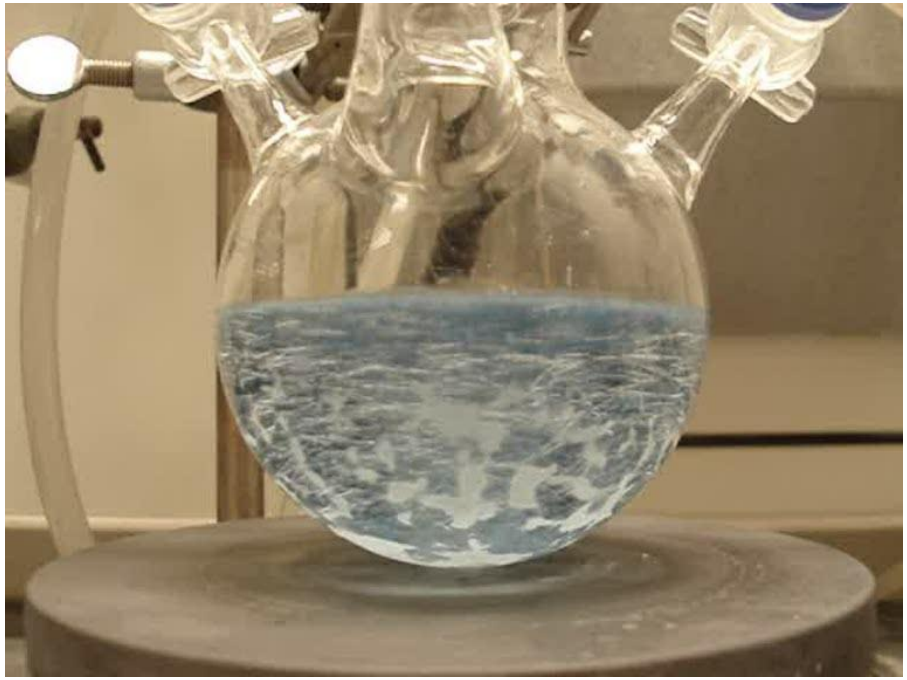
10 nm

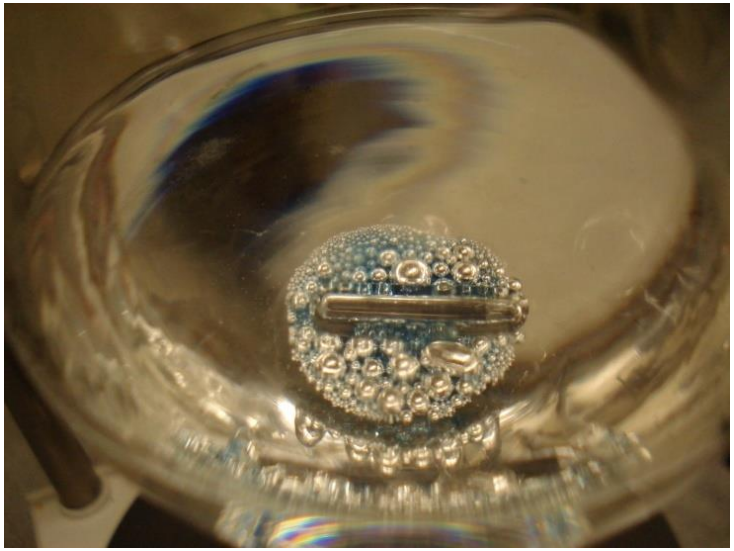
Intercalation - Reduction







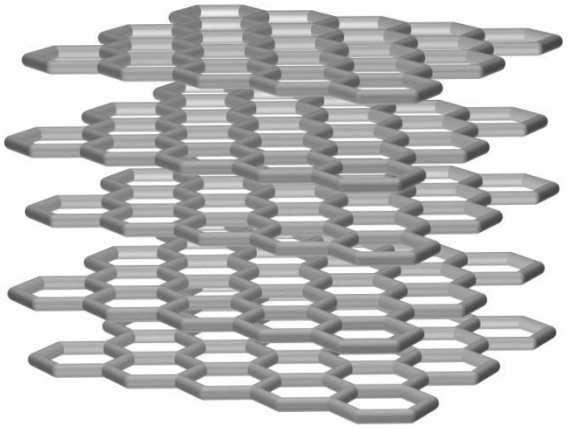




$$K \xrightarrow[DME]{} [K(DME)_n]^+ + e^-_{(solv.)}$$

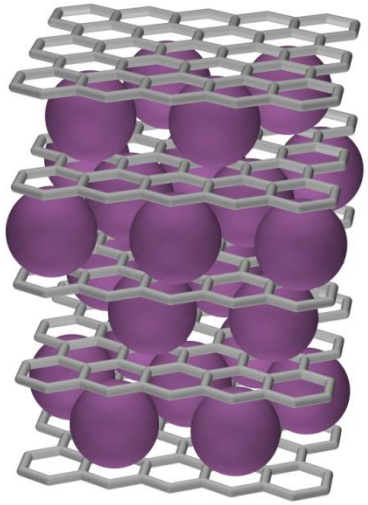
$$2e^-_{(solv.)} + K^+ \rightleftharpoons K^-_{(solv.)}$$

Reduction – Arylation

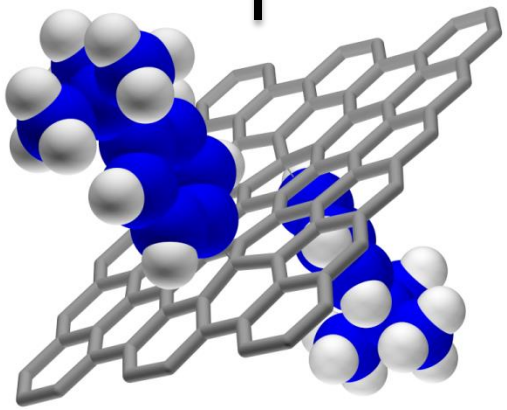


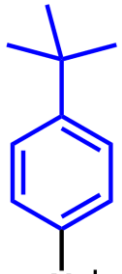
NaK_3

3d, 300K

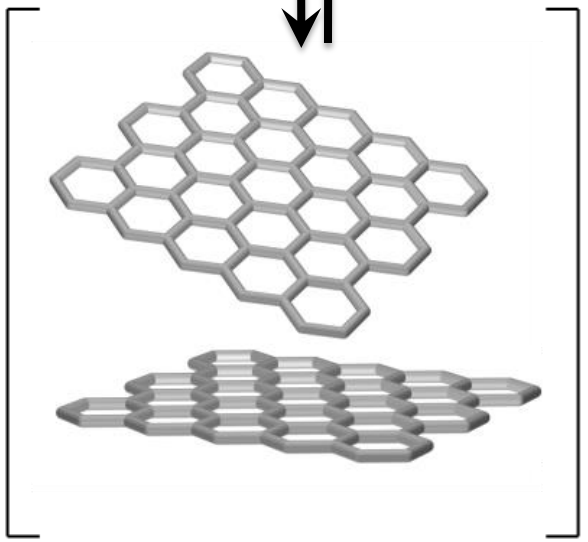


Δ

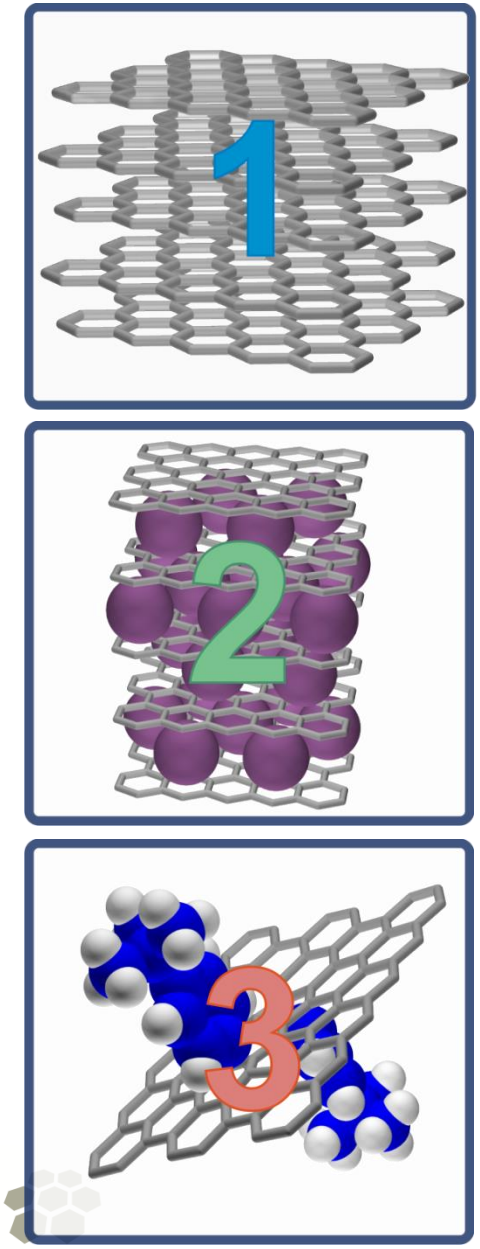


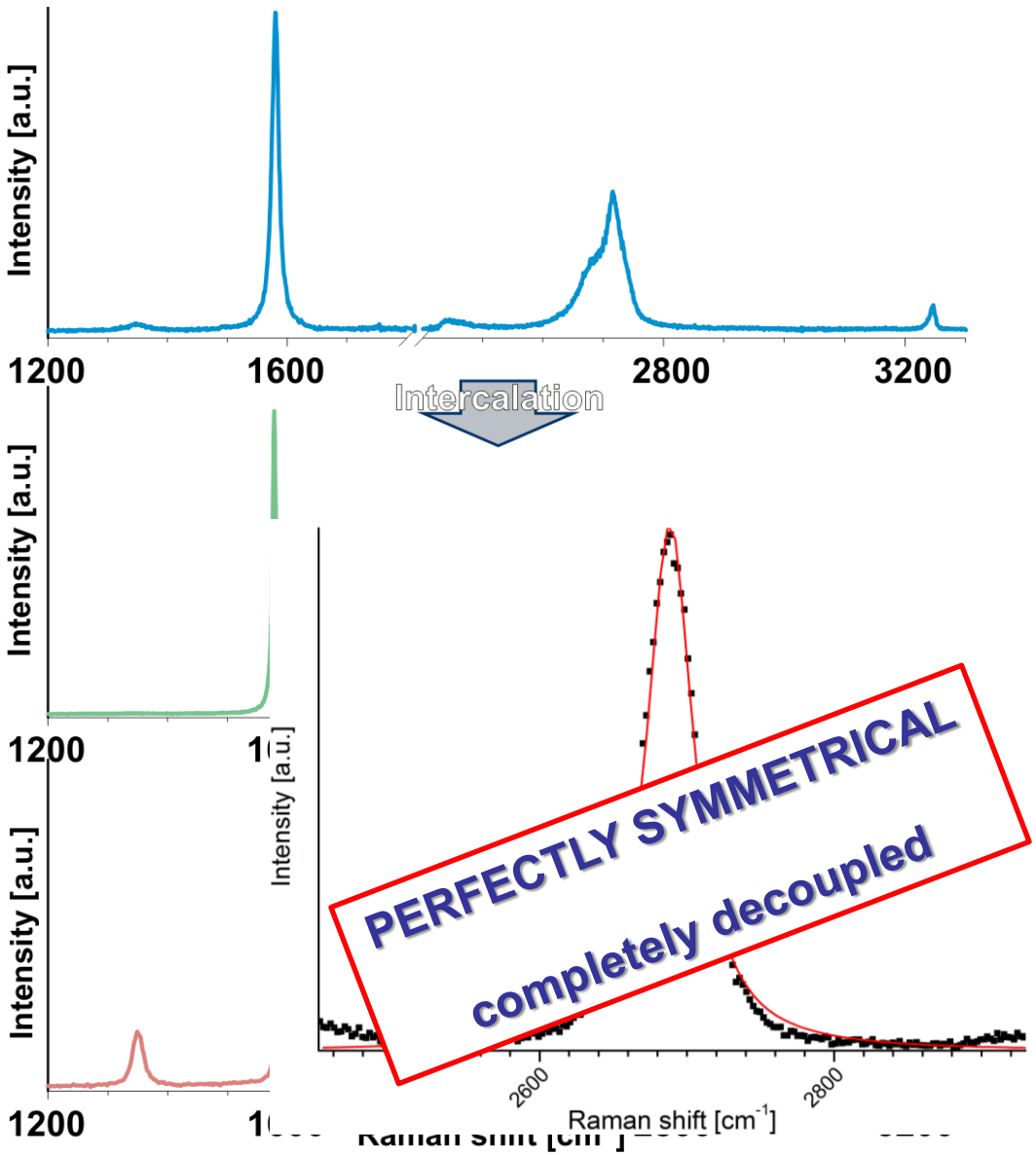


- N_2

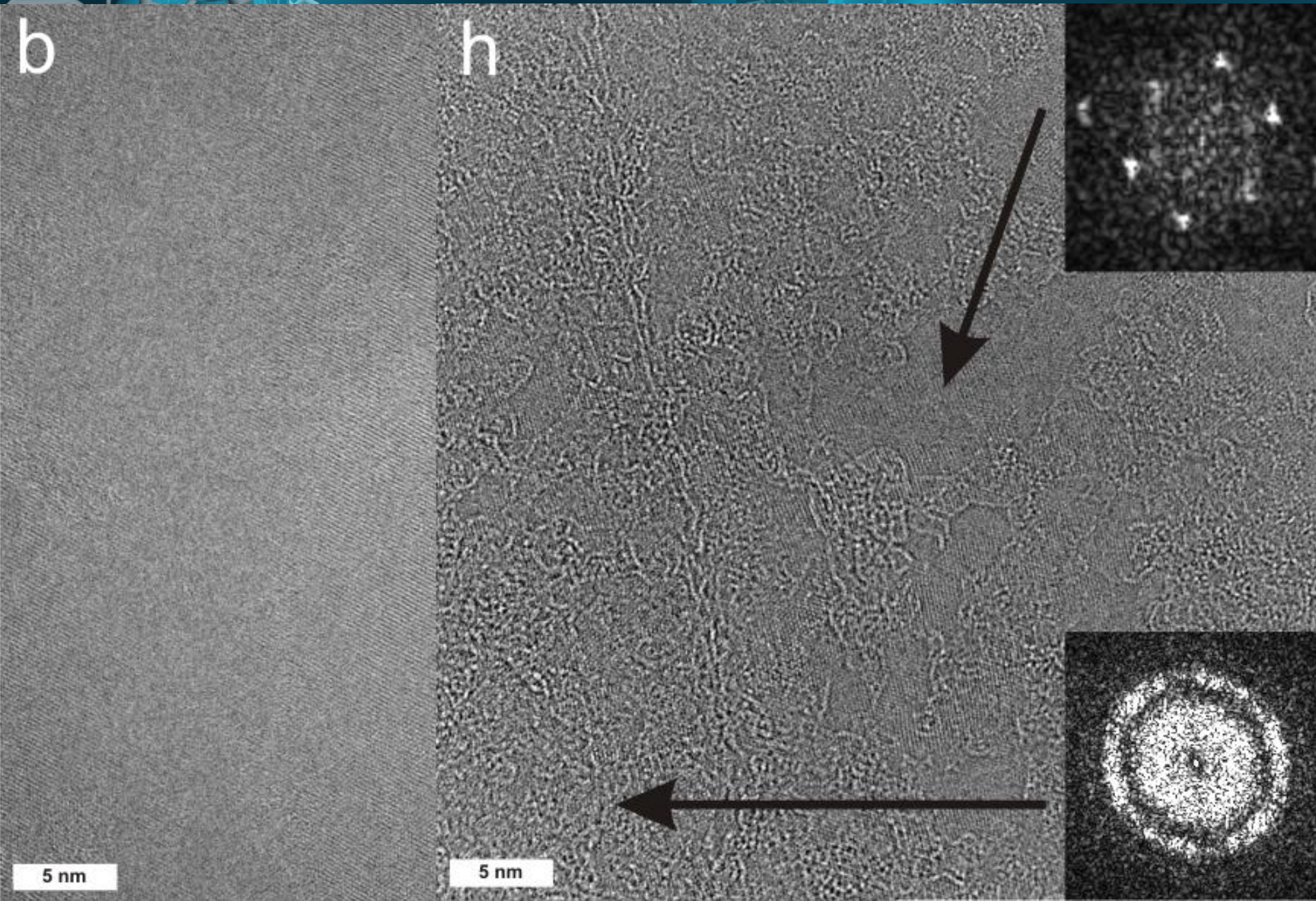


Deposition – Raman Spectroscopy

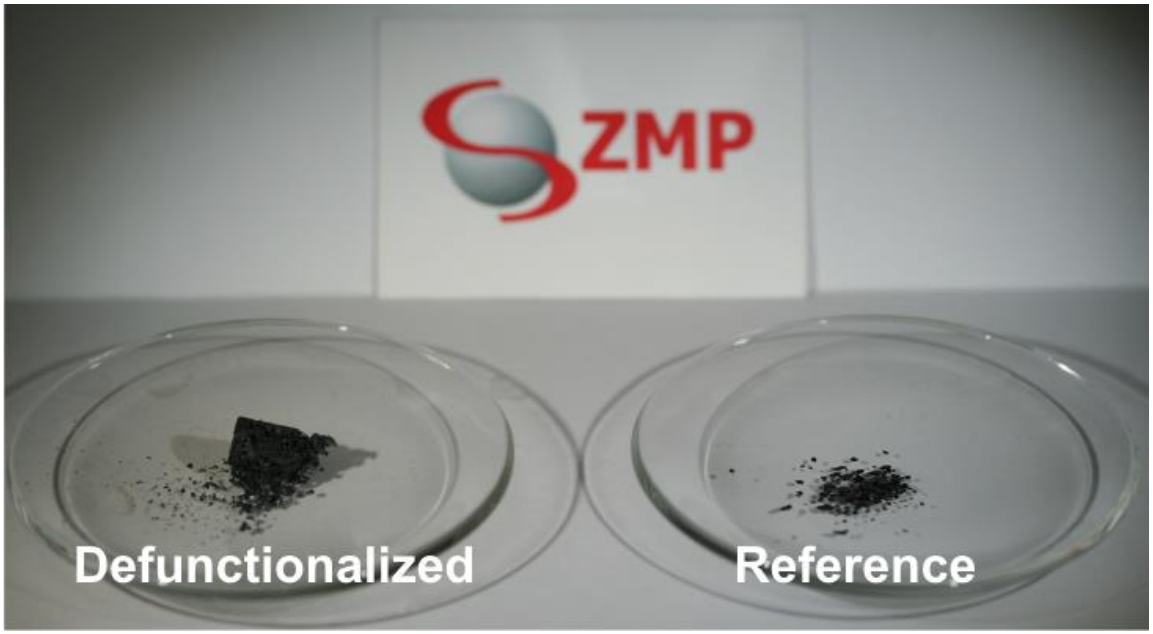


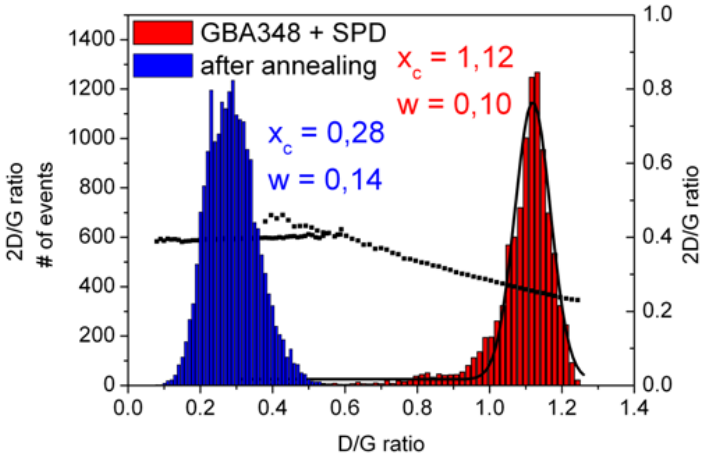


HRTEM

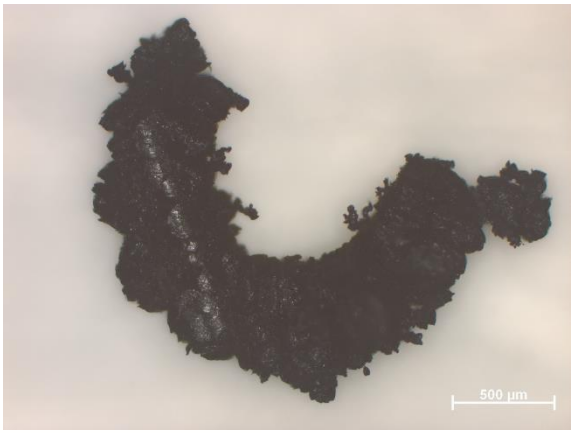


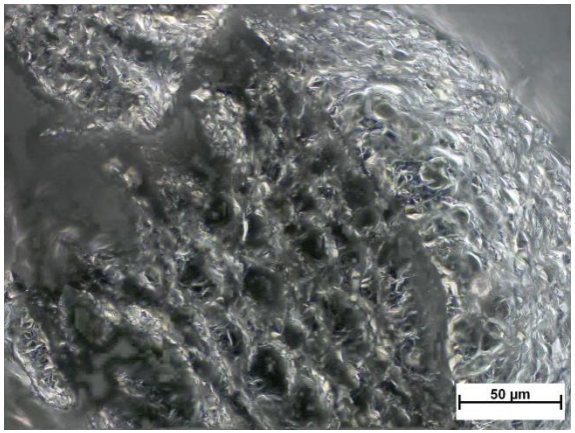
Thermogravimetric Analysis

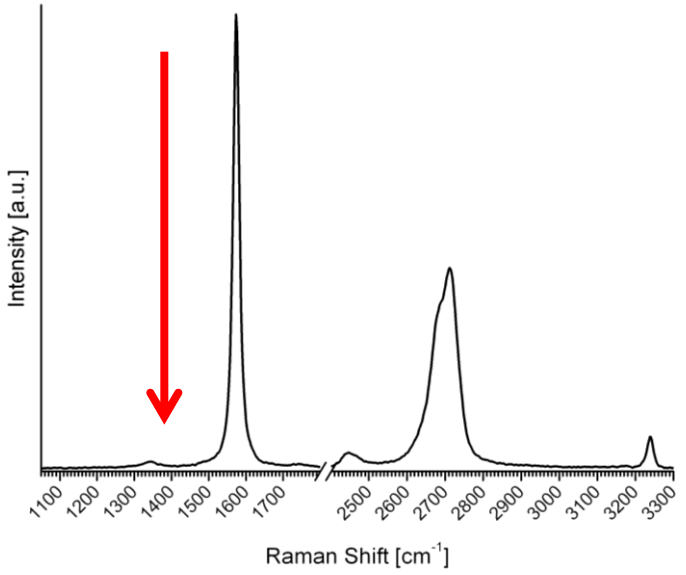




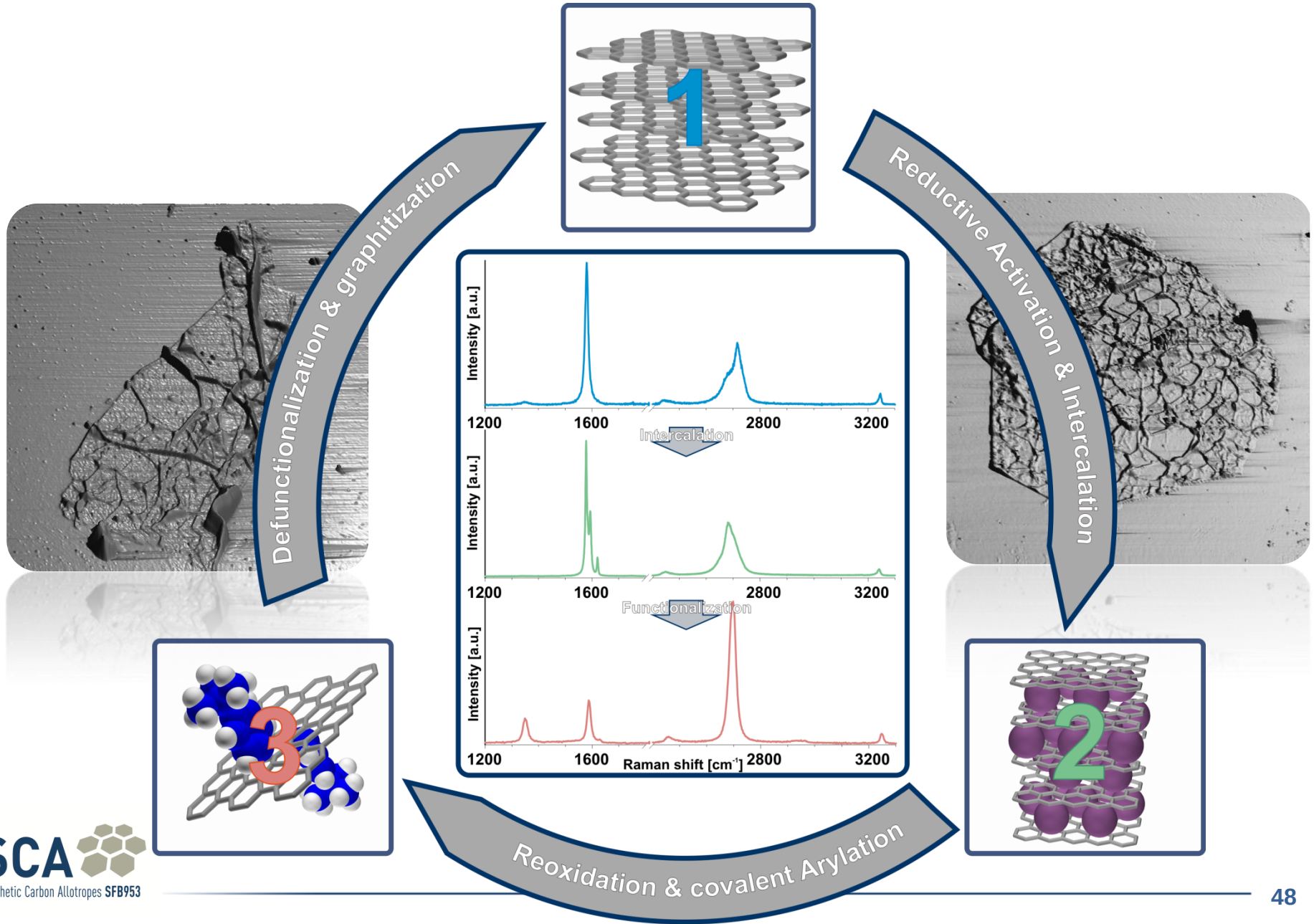
No D-band signal



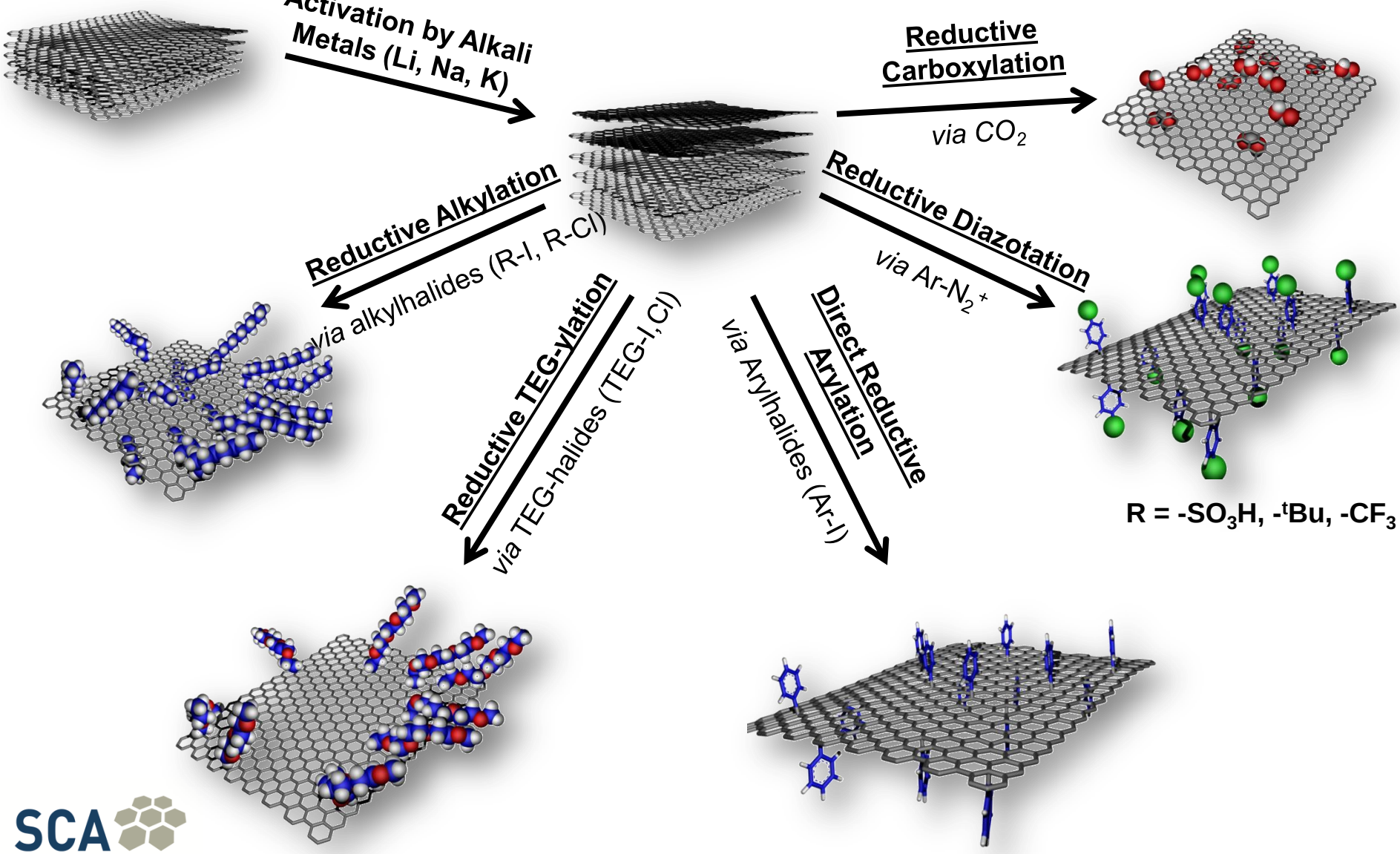




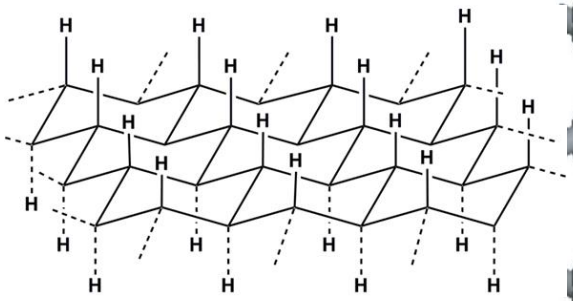
Reversible Functionalization

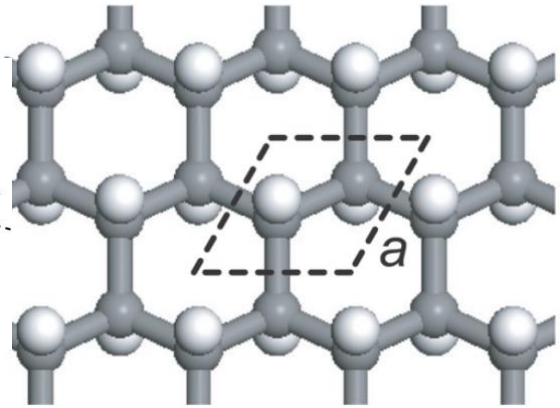


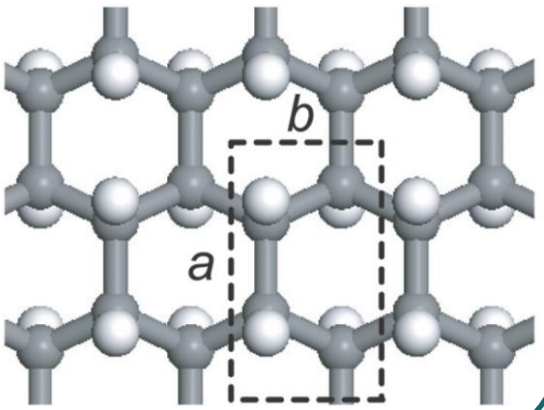
New Functional Graphenes



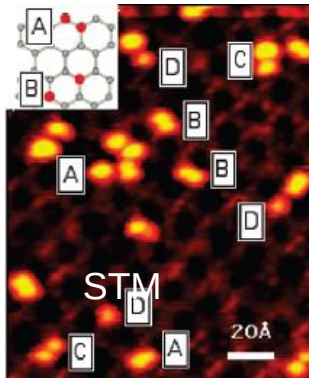
Hydrogenation: Towards Graphane





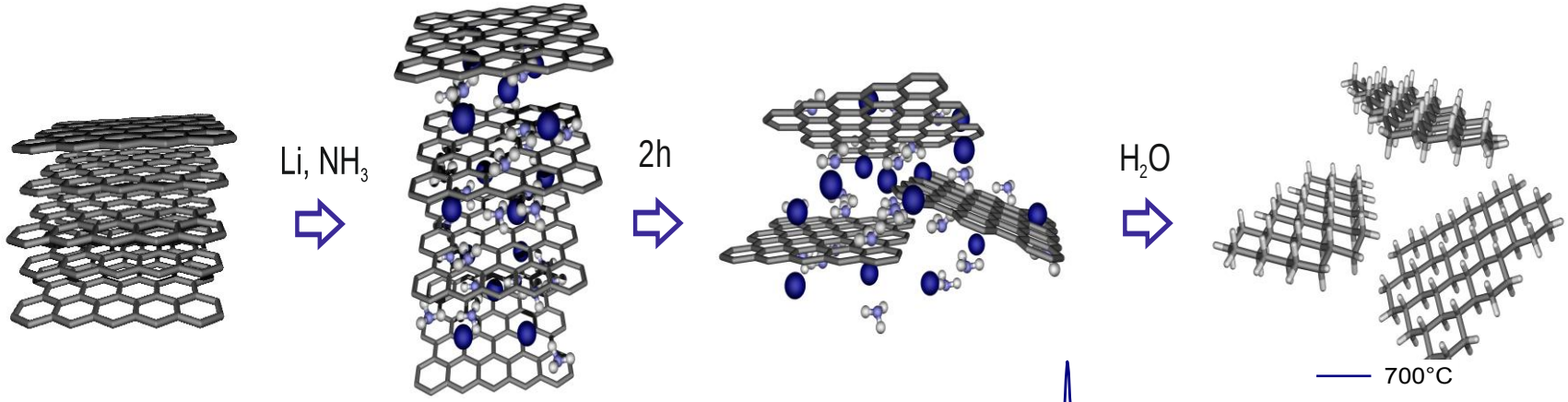


- **production**
- hydrogen plasma
- hydrogen + heat + pressure
- hydrogen + catalysator + pressure
- chemical hydrogenation?

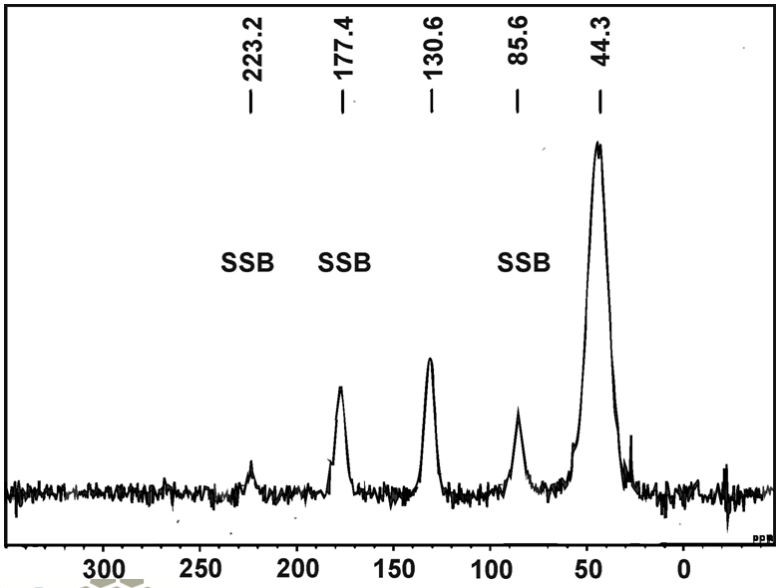


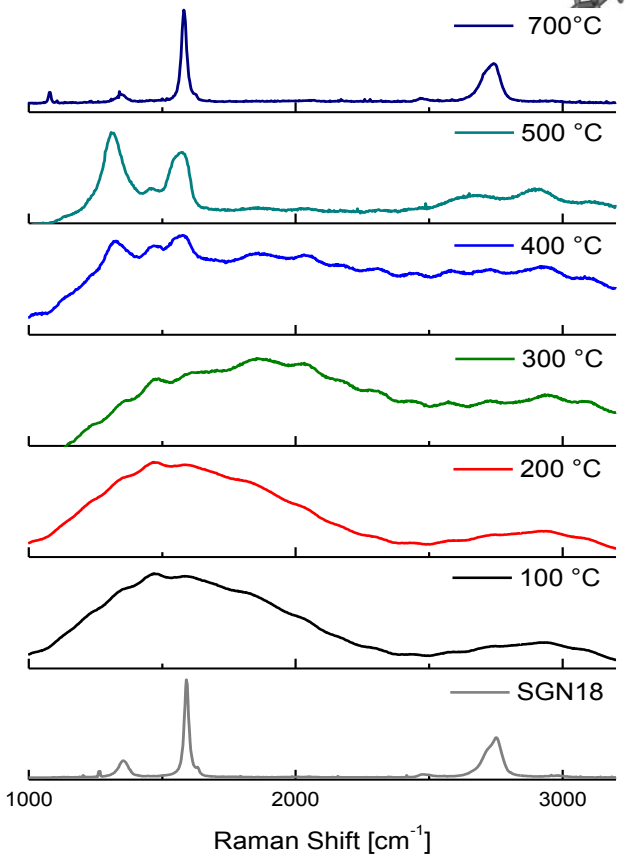
M.Z.S. Flores et al., *Nanotech.*, **2009**, *20*, 465704; D. Martindale, *Discover Magazine*, **2002**; J.O. Sofo et al., *Phys. Rev. B ,* **2007***, 75*, 153401

Birch Hydrogenation

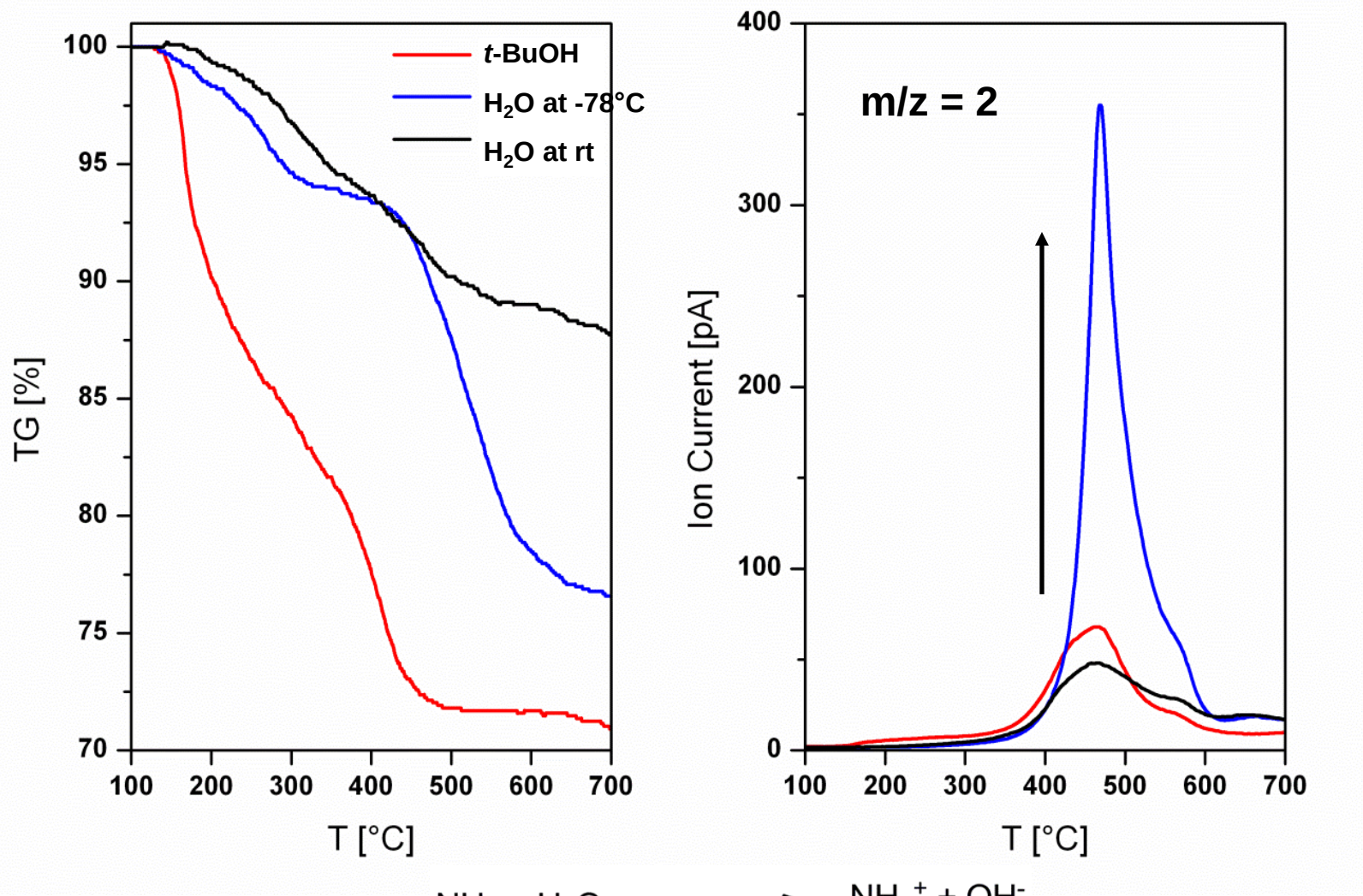


CP-MAS ^{13}C-NMR



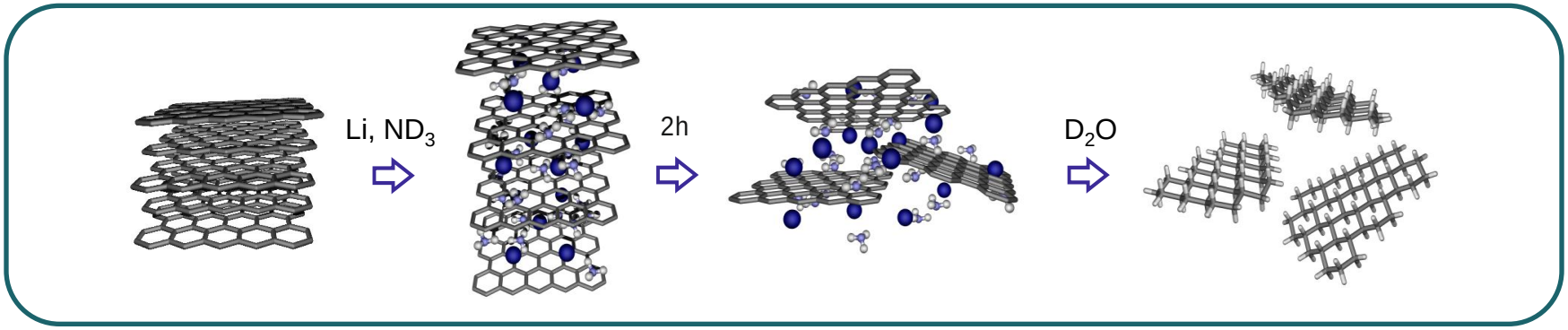


Hydrogenation of Graphene: TGA MS

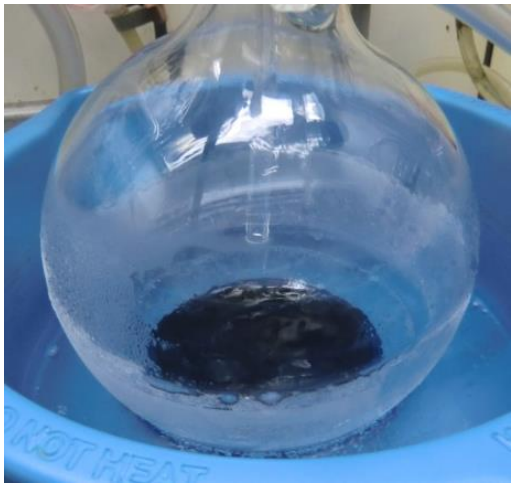


$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

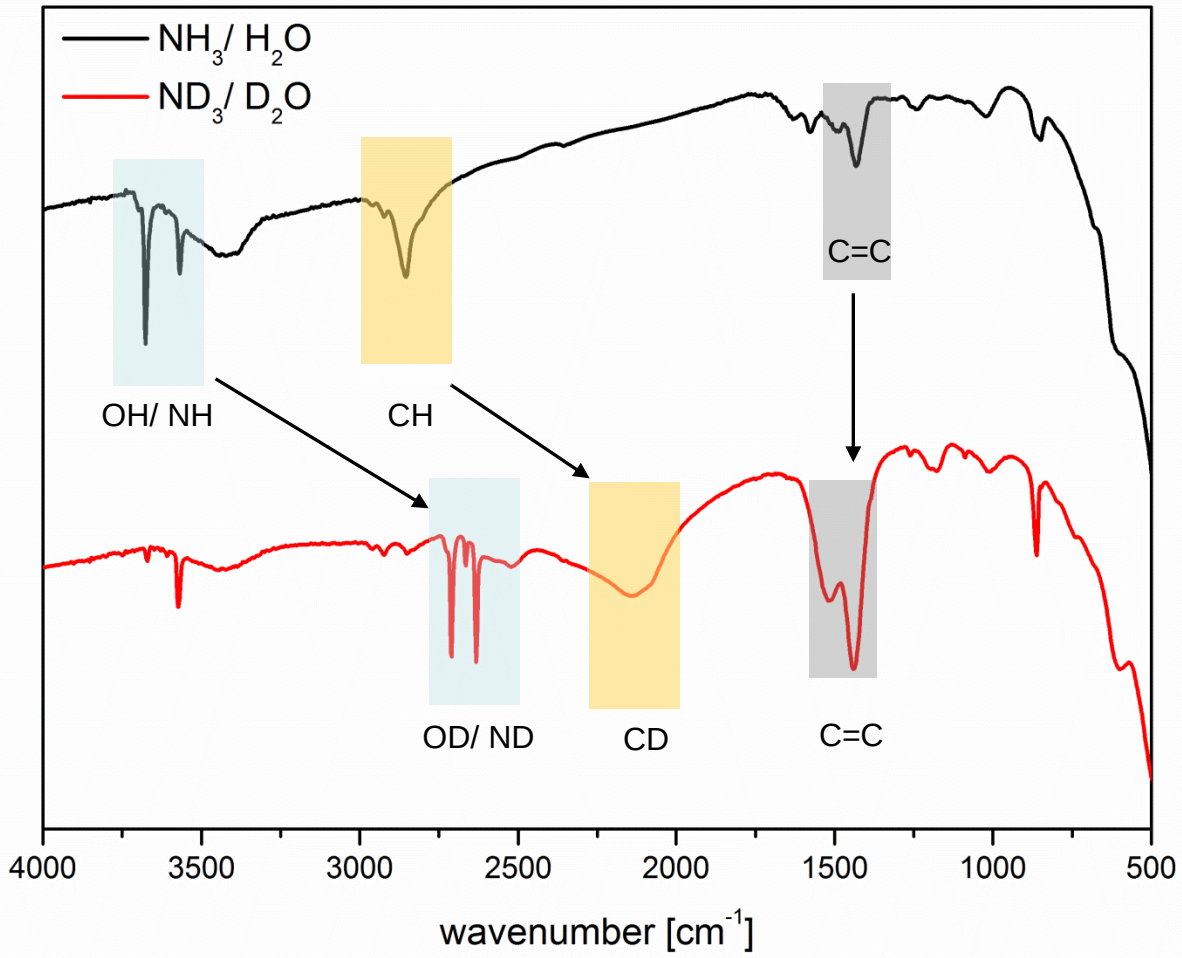
Deuteration of Graphene



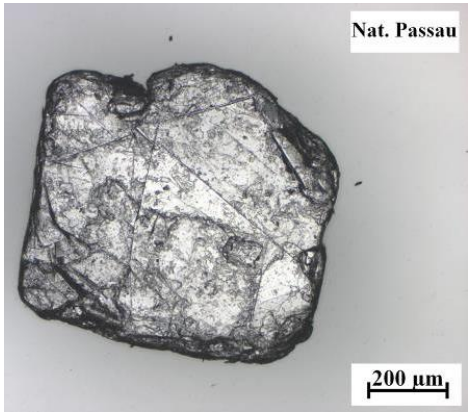
production of heavy ammonia

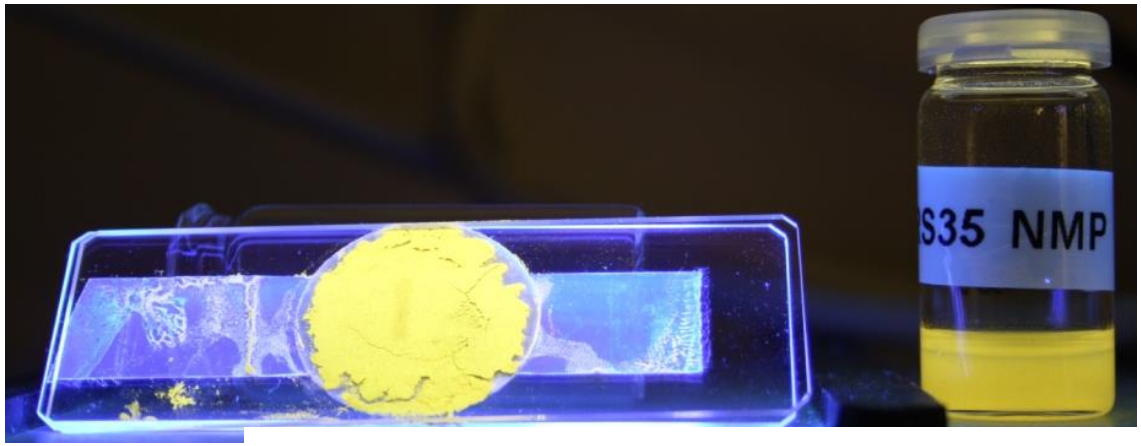


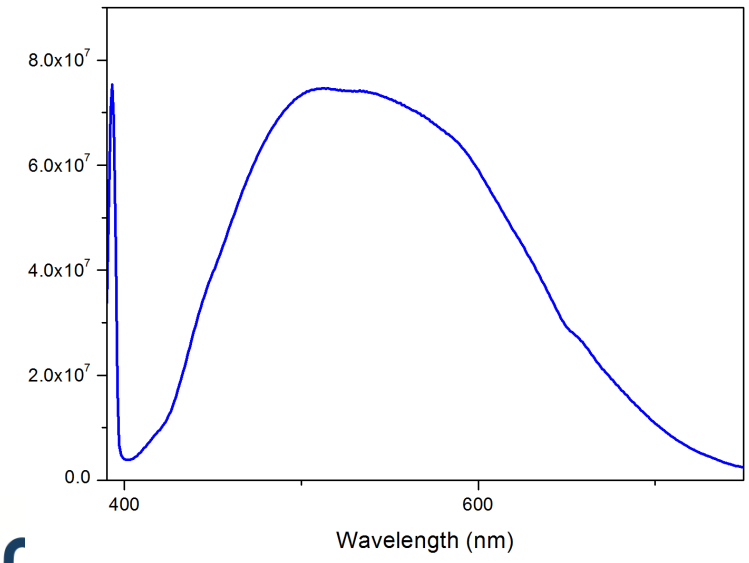
Deuteration of Graphene - IR

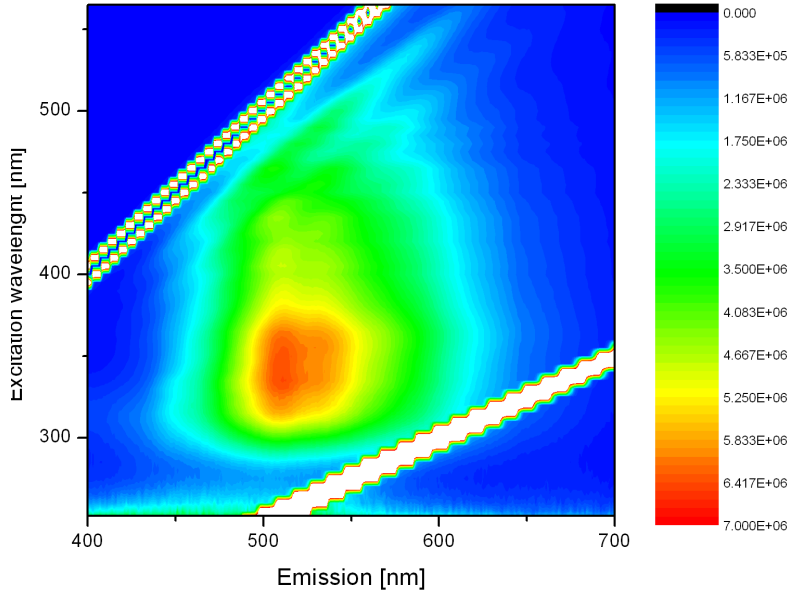


Hydrogenation









Thank You!


Thank you for your attention!